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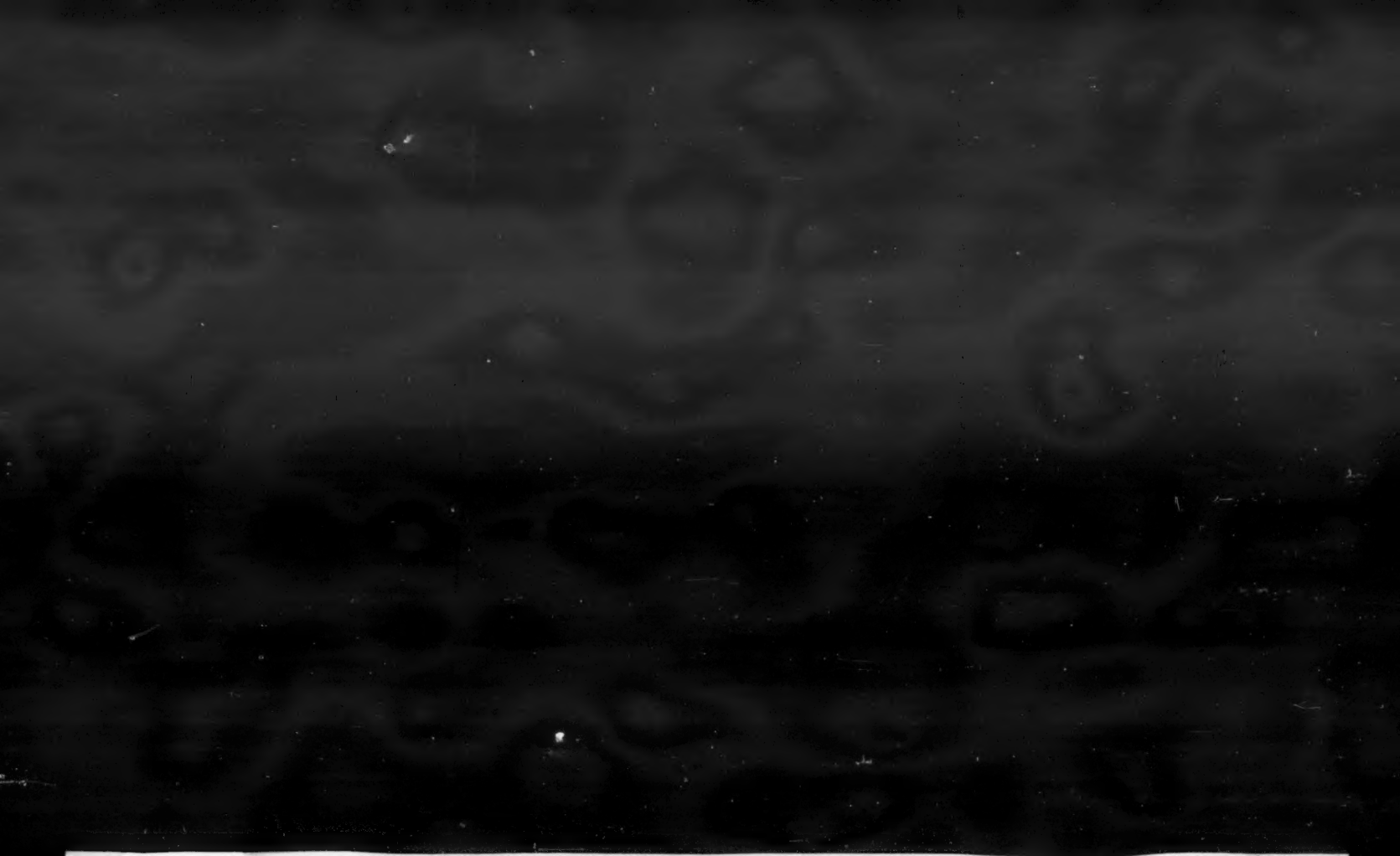

THE

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

ART. XXVI.—*The Lime-Silica Series of Minerals:** by ARTHUR L. DAY and E. S. SHEPHERD, with Optical Study by FRED E. WRIGHT.†

Part I. Introductory.

ANYONE who has followed the work of the eminent Norwegian scientist, Prof. J. H. L. Vogt, during the past three or four years, must realize that an extraordinarily effective weapon has come into the service of petrology, the full power of which cannot at once be understood or appreciated. We refer to the methods and established generalizations of physical chemistry. The older science of chemistry has made such strides under these new theories of solutions that we really have little more to do than to apply them ready-made to our own problems, like a smooth and powerful machine tool of guaranteed effectiveness. Mineral solutions, as Bunsen long ago maintained, are after all only chemical solutions over again with slightly different components and a different, a very different, range of temperatures and pressures. There is no need to disparage the difficulties involved in operating at high temperatures and under great pressures; they are very great, probably even greater than most of us appreciate, but they are certainly not insuperable, and when they are overcome, not only will a new era in the science of petrology have been inaugurated but an important return service will have been rendered to physics and physical chemistry in extending the scope of their generalizations.

There is, therefore, no question of where to begin. Roozeboom, Vogt, and many others have seen and appreciated and indicated to us with great clearness the various ways in which

*Full text of a paper of this title read before the American Chemical Society at the Ithaca meeting, June 28, 1906.

† The authors are indebted to Prof. A. C. Gill of Cornell University for a number of microscopic examinations of our earlier products, and for many helpful suggestions.

mineral and rock formation can now be competently studied. The question is now, rather, how much of it all can we actually carry out? Vogt has already shown us,* in a paper published only a few months ago, that a great deal can be accomplished by a judicious treatment of existing observations, particularly the more trustworthy of the mineral and rock analyses, when combined with extensive field experience.

It has been the purpose of this laboratory to attempt this task by a direct application of the principles and methods of quantitative physics and chemistry, or, in a word, to study mineral and rock formation by direct measurement at the temperatures where the minerals combine and separate like the solutions of ordinary chemistry under ordinary conditions. We further determined, wherever possible, to prepare chemically pure minerals for this purpose in order that such conclusions as we might reach should not be dependent upon dangerous assumptions regarding the harmless character of the five or ten per cent of "impurities" not infrequently present in hand specimens from natural sources. It is at once obvious that in order to succeed, the first experiments must be restricted to the simplest reactions, and that these will not always be the most important or the most interesting, but the results will always be in definite terms and final when the materials used are pure. Furthermore, the accumulated experience obtained from simple cases will safely and surely lead to successful methods of a scope to meet the more complicated problems of rock formation.

This plan was really entered upon several years ago in a small way and with very limited resources. The first paper, which was published in 1904-05, contained a laboratory study of a typical isomorphous pair, the soda-lime feldspar series, carried out in the spirit of the above plan. The second, which appeared in February of the present year, was a very careful study of enantiotropic mineral inversion between the mineral wollastonite and the pseudo-hexagonal form which has been obtained by several observers but which appears not to have been found in nature. The present paper, which is the third of the mineralogical series, undertakes to carry through a fairly complete set of measurements upon a typical eutectic pair—the lime-silica series. It is still incomplete in some particulars, notably at the ends of the series. Mixtures very rich in lime possess temperature constants which are beyond the reach of existing apparatus, while on the silica side the extreme viscosity and consequent inertness which were encountered in the soda feldspars, effectually veil or prevent the development of the phenomena which occur there. Some approximate measurements have been made even in these

* J. H. L. Vogt, Physikalisch-Chemische Gesetze der Krystallisationsfolge in Eruptivgesteinen, Tschermak Min. u. petr. Mitth., xxiv, 437, 1906.

regions (represented by dotted lines in the diagram fig. 3), but they have not the same accuracy as those portions of the curve which are represented by full lines. All the mixtures used were prepared with the greatest care and were chemically pure within one or two tenths of one per cent.

Lime-Silica Minerals.—Of the lime-silica series only one well-defined mineral is known—wollastonite—which when melted usually crystallizes in a pseudo-hexagonal form of the same composition. This mineral has already been carefully studied by Allen, White, and Wright,* and the relation between the natural mineral and its second crystal form thoroughly cleared up. Pursuing the conventional methods of reasoning, we might also expect to have an intermediate mineral for the trisilicic acid, $2CaO,3SiO_2$ an åkermanite analogue, $4CaO,3SiO_2$; an orthosilicate, $2CaO,SiO_2$, and a tricalcic silicate, $3CaO,SiO_2$. All of these minerals are deducible from the various hypothetical silicic acids. We have undertaken to prepare and study the entire series of mixtures of lime and silica.

Boudouard's Measurements.—So far as known, there has been only one serious attempt to determine the constitution of this series of minerals.† According to Boudouard, the freezing point curve for the lime-silica minerals consists of four eutectics and three maxima (compounds), the maxima corresponding to the metasilicate, the orthosilicate and the tricalcic silicate. Unfortunately, the method used by Boudouard was a very inaccurate one. He prepared small cones of the various mixtures and placed these in a furnace alongside of Seger cones. The furnace was then heated and allowed to cool down again, after which the crucible was opened and the cone observed to see whether or not the mineral had melted. It is a common method in industrial practice, but has rarely been thought accurate enough for original determinations.

This method is peculiarly unsuited for such investigations for several reasons: Suppose the mixture to contain an eutectic with a greater or less excess of one of the components. The cone would begin to weaken as soon as the eutectic began to melt, and its further progress would be governed entirely by the relative quantity of eutectic present and its viscosity *after melting*. No information whatever regarding inversions in the solid or of the component in excess could be obtained, and errors of more than 500° would certainly occur (in fact did occur in Boudouard's case) in the interpretation of the softening temperature in some parts of the lime-silica curve. Let us illustrate by a perfectly obvious hypothetical case (fig. 1): Assume first that the melting-points change rapidly following a steep liquidus AB

* E. T. Allen, W. P. White and Fred Eugene Wright, "On Wollastonite and Pseudo-Wollastonite, Polymorphic Forms of Calcium Metasilicate," this Journal. xxi, 89, 1906.

† Boudouard, Journ. Iron and Steel Institute, 1905, p. 339.

(see also fig. 3, curve DE). The amount of eutectic in concentrations X and Y will be so great as to soften the cone long before the melting-points Z and W are reached. If, on the other hand, the liquidus slopes gently (AC), the amount of liquid eutectic as compared with the solid phase is smaller and the temperature of softening of the cone will approximate more closely to the change in melting-point.

Furthermore, if the cones are made up from the initial components ($CaCO_3$ and SiO_2, for example), the heat of combination is liberated as the cone approaches the melting temperature and raises the temperature of the cone above that of the furnace, producing sudden fusion of which the neighboring Seger cone can receive no record.

Incidentally, one finds here the explanation of Hoffman's experiments* on the temperature of formation of slags. Contrary to the statement that the "temperature of formation is above the

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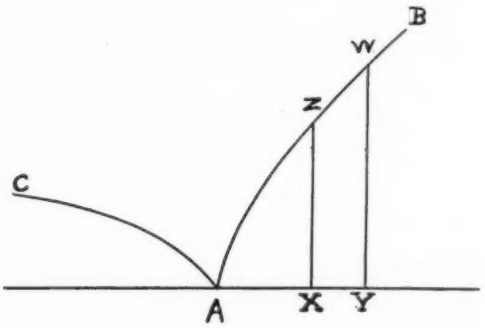

temperature of fusion," just the reverse is true. Under normal conditions these mineral combinations occur at temperatures lower than the melting point, the exceptions occurring only when the materials are so coarsely ground or poorly mixed that combination is retarded until the melting point of the slag is passed. The orthosilicate of calcium is a very good instance of the formation of a compound below its melting temperature. We shall show later that while this compound melts at about 2080° C., it is possible to prepare it below the melting point of platinum, in fact in platinum vessels, by heating the finely ground material in the Fletcher furnace, regrinding, mixing and reheating. By this process it is possible to obtain a compound which gives the optical tests for the orthosilicate and is entirely without free lime or silica.

Apart from the criticism which this particular application of cones appears to us to deserve, it is also well known that the

*H. O. Hoffman, Trans. Amer. Inst. Min. Eng., xxix, 682, 1899.

time factor is always very important in dealing with a Seger cone. Boudouard himself states (p. 343): "A very small difference in temperature, or *a few minutes additional heating*,* often suffices for the softening stage to pass into one of complete fusion." If this statement was made understandingly, the method merited rejection by Boudouard himself. Furthermore, the use of Seger cones for exact work will always be unsatisfactory because it depends upon the judgment of the operator to say when a cone has "fallen" sufficiently to be considered melted, and different observers almost always obtain widely different results under like conditions. As has been pointed out by Day and Allen,† any method of measurement which is not based upon some reasonably sharp physical change must be expected to give different results in different hands.‡ Suppose

* Italics are ours.

† Arthur L. Day and E. T. Allen, "The Isomorphism and Thermal Properties of the Feldspars;" this Journal (4), xix, p. 93, 1905. Zeitschrift f. Phys. Chem. liv, p. 1, 1905. Publication of the Carnegie Institution of Washington, No. 31.

‡ Since the text of this paper was written, a very recent paper by Doelter (C. Doelter, "Die Untersuchungsmethoden bei Silikatschmelzen," Sitzungsber. d. Wien. Akad. cxv, 1, May, 1906) has come to our attention in which he reaffirms his confidence in and preference for subjective methods for the investigation of silicate solutions,—more particularly the viscous silicates. This question of methods of attack in problems of wide scope and considerable difficulty is not an academic one; it is a matter of the very first importance, particularly in view of the increased attention which is coming to be paid to the minerals as solutions. We have preferred to avoid subjective methods wherever possible on the general ground that no observation so made is exactly reproducible. Subjective observations are therefore always much more satisfactory to the observer than to any one else. Prof. Doelter has probably had a greater and more varied experience in the observation of mineral melting points than anyone now living, and he is therefore able to form consistent judgments upon the changes which he observes. But even under his exceptionally competent hand we have seen the "melting points" of the feldspars rise a little higher each year in his successive publications upon the subject, and the feldspars are very viscous minerals of the type to which he finds the optical methods especially adapted.

Doelter then criticises the thermoelectric methods in use in this laboratory on the ground of inexactness, i. e., because the recorded time-temperature curves contain no period of absolutely constant temperature, although he appears to be very familiar with the fact that the phenomena themselves are not sharp. This seems to be unfortunate and unproductive criticism. Under fair conditions a phenomenon is obviously the same, whether observed by looking at the charge or by exposing a thermoelement in it. If the supposed melting "point" does not occur at a point, it cannot be recorded as such. So far from failing in its purpose, therefore, the thermoelement has revealed to us a hitherto unfamiliar phenomenon with great fidelity. Our principle in the choice of methods is therefore diametrically opposed to Doelter's. If the change of state were sharp and well marked, it would really matter very little how it was determined. If, on the other hand, it is a slow change, we should greatly prefer the unprejudiced record of a thermoelement if it could be obtained. Nothing is so difficult of observation or gives rise to so much difference of opinion between observers as a slow-moving phenomenon. An interesting example of this is to be found in this (Doelter's) paper itself (p. 12). Nearly all observers of the constants of silicates are now completely agreed that the glasses are merely undercooled liquids which of course have no melting point but change *continuously* from a hard amorphous to a soft

this method were to be applied, for example, to the determination of the melting temperature of orthoclase or albite, or even pure quartz, which have been shown to possess a viscosity entirely comparable in magnitude with the rigidity of the solid crystalline mineral; almost any conclusion could have been reached under these conditions.

It is stated by M. Boudouard, for example, that all mixtures of lime and silica between 30 and 90 per cent of lime melt below 1500°. This certainly cannot be the case. Pure orthosilicate of calcium when heated in a platinum crucible will stand without showing the slightest trace of melting while the platinum containing vessel melts down. The temperature must therefore be at least as high as the fusion point of platinum (1720°). We found no lime-silica mixtures richer than 60 per cent in CaO which could be melted in platinum vessels.

Apart from the uncertainty in the temperature measurements offered by Boudouard, we shall undertake to show in its proper place that there is no pure lime-silica compound corresponding to åkermanite and no tricalcic silicate. We are, therefore, somewhat at a loss to explain in any satisfactory way how the published curve which has attracted so much attention in England was really obtained.

Part II. Experimental.

In this kind of investigation it is always desirable to begin with a careful determination of the physical properties of the pure components, although in the present case it must be admitted that this was the most inaccessible and difficult portion of the field over which we worked.

amorphous condition. The use of subjective methods has misled Prof. Doelter into picking out points upon these curves to which he attaches great importance in the determination of eutectics.

Apart from this general criticism, the particular optical methods which Doelter employs appear to us rather limited in scope for the work they will be required to perform. In the case of a mineral combination which is neither an eutectic nor a pure compound, they are open to all the objections of Boudouard's method (see above) and furnish no trustworthy information whatever. It is also difficult to see how they can be used effectively to determine unknown conditions of equilibrium. Doelter's method 4 (p. 6, loc. cit.), in which he places greatest confidence, appears to us to promise immediate and serious difficulties of another kind. It consists in observing directly with the microscope tiny grains of the substance to be studied as they lie upon a tray of amorphous silica (quartz glass) in the furnace. The glass tray, which is, of course, also heated, is in very unstable equilibrium and therefore ready to enter into solution with almost any oxide or silicate in contact with it at relatively low temperatures, and to produce what may appear to be a melting point but which of course has no necessary relation to that of the pure substance examined. Joly's old method of examining mineral fragments on a platinum strip was much more trustworthy for melting point work, although inversions in the solid state could perhaps be advantageously studied in the new apparatus.

For these reasons it does not seem to us wise to employ the subjective methods when others which are reproducible by any observer are available.

Lime.—Calcium oxide melts at a temperature so high that it is not yet possible to make a satisfactory determination of its melting point. It can be fused in the electric arc under favorable conditions to a clear liquid of low viscosity which crystallizes readily into a well developed cubic structure. Near its fusing temperature, lime either becomes quite volatile or the carbon of the arc reduces it to the metal, which volatilizes and is immediately reoxidized outside of the heated zone. We are unable to offer conclusive evidence in favor of the one hypothesis or the other, but the fact that pure lime at 2000° shows no signs of a high vapor pressure points rather to the second explanation as the correct one.

For experiments with lime fusion, we obtained some artificial graphite* practically free from all impurities, so that no contaminating substance was introduced into the fused lime from the electrodes. To further guard against possible contamination, only that part of the cake which formed above the (horizontal) arc was used in determining its physical properties.

Density of CaO.—The density of fused calcium oxide was determined as follows: A selected portion of the crystalline mass was finely ground, ignited to drive off adsorbed water, and weighed in carefully dried turpentine after the method of Day and Allen. The results are not in very good agreement, due probably to the difficulty of weighing out the product without its becoming superficially hydrated or absorbing CO_2.

Fused CaO. H_2O at 25° = 1.
3·313
3·307
3·329
Mean density, 3·316 (25°)

This crystallized lime is much less readily attacked by water than is the amorphous oxide. It is, however, not indifferent to water. Five grams of the crystals when ground and mixed with a small quantity of water in a test tube scarcely raised the temperature at all, but upon standing for some five minutes, the charge exploded with considerable violence. Unpowdered blocks of the crystalline oxide when placed in cold water dissolved slowly without appreciable heating. Hot water attacks them more rapidly, but the action of the water is slow in both cases as compared with the amorphous lime.

The hardness, according to Mohs's scale, is between 3 and 4.

Silica.—The melting temperature of silica has been variously estimated at from 1200 to 2000°, but so far as known no

*Prepared by the International Acheson Graphite Company, Niagara Falls, New York.

careful determination of it has ever been made. Since this oxide melts to an extremely viscous liquid, attempts to determine the melting temperature by observing the softening of the charge are wholly misleading. The molecular deorientation proceeds very slowly, extending over a considerable range of temperature, as albite and orthoclase have been found to do,* but with the disadvantage that this temperature region is too high to be reached with a thermoelement, and no other method of temperature measurement possesses sufficient sensitiveness in this region to locate the melting temperature by the heat absorbed during slow fusion. Determinations of the freezing-point are out of the question, owing to the inertness of the viscous melt.

An approximate determination of the melting temperature was made in this way: A gram or two of finely powdered quartz was placed in a small iridium crucible and heated in an iridium tube furnace (see p. 286). (Experience has shown that melting and inversion phenomena in very viscous substances take place much more readily if the material is finely divided.) A tiny fragment of platinum foil was then laid on the top of the charge and the furnace slowly heated until the foil was observed to melt. Upon removing the charge from the furnace and examining it microscopically, evidence of fusion was found throughout the mass. The crystal grains had inverted to tridymite and the superficial liquefaction had caused them to sinter tightly together, but no displacement of the grains had taken place. At the temperature of melting platinum, therefore (1720°), silica shows positive evidence of fusion. Other similar charges were then prepared and the operation repeated with longer exposures and temperatures slightly below the melting point of platinum, the temperatures being measured with a Holborn-Kurlbaum optical pyrometer† focused on the platinum fragment. By repeating this process at short temperature intervals and with about 20 minutes exposure, melting was definitely established as low as 1625° C.

The iridium furnace is unfortunately not adapted for long-continued heating, and the platinum coil furnace will not reach this temperature, so that an effort to discover a definite temperature below which the solid is stable and above which it will melt if given time enough, was abandoned. If the heating is moderately rapid, the crystalline solid will persist far above the melting point of platinum; if slow enough, it liquefies completely at 1625° or even lower. It is probably a fair assumption, that pure silica begins to melt at about 1600,° and will continue to complete fusion if given time enough,—

* Day and Allen, *loc. cit.*

† Holborn and Kurlbaum: Ann. d. Phys. x, p. 225, 1903.

above that point the higher the temperature, the more rapid the melting. A charge of quartz was heated for a long time in a platinum furnace at 1555° without producing a trace of fusion.

There is little satisfaction in pursuing an inquiry of this kind. As has been stated elsewhere with reference to an entirely similar case,* the term "melting point" does not appear to be well applied to cases of this character, in which the crystalline structure persists for days or weeks at temperatures above the point where melting begins.† If the change of state is to be defined by the absorption of heat, and the absorption of heat extends over a wide range of temperatures and conditions, our forms of expression should be revised somewhat to include these hitherto unrecognized cases.

Tridymite.—The relation between tridymite and quartz appears to be a simple one, although the literature of the subject is unsatisfactory. But few trustworthy observations have been recorded and the conclusions drawn from them are vague and contradictory. So far as known, quartz has never been crystallized as such from mineral fusions except where catalyzers were present. Tridymite has probably been obtained by several individuals through the accidental crystallization of fused silica vessels,‡ but no especial attention appears to have been given to the circumstances in which it occurs, and its identification has not always been positive.

Like the melting temperature, the inversion of quartz to tridymite and the crystallization of fused silica are very difficult phenomena to study, owing to the extreme inertness of the material, but a number of experiments have been success-

* Isomorphism and Thermal Properties of the Feldspars, Publication 31, Carnegie Institution of Washington, p. 74 (3).

† Doelter has recently offered a new general classification of silicates (loc. cit. p. 3): "Einfacher konstituierte Silikate (Gruppe A) haben scharfen Schmelzpunkt, geringere Viskosität und grösseres Kristallisationsvermögen. Komplexere Silikate (Gruppe B) haben ein grosses Schmelzpunktsintervall, grosse Viskosität, geringere Kristallisationsgeschwindigkeit."

Such information as we have been able to gather in our work with pure minerals does not substantiate this generalization. We have encountered no mineral more viscous than quartz, which has the simplest of compositions. Anorthite, wollastonite and diopside differ radically in simplicity of formula but melt and crystallize at very nearly the same rate and with very nearly the same sharpness.

‡ Prof. Dr. L. Holborn of the Physikalisch-Technische Reichsanstalt; Dr. M. Herschkowitsch of the firm of Carl Zeiss in Jena; Dr. Küch of the firm of Heraeus in Hanau; and the Rev. Theodor Wulf, S. J., formerly of Göttingen, in the preparation and use of quartz glass vessels have noticed that the glass devitrifies at high temperatures in the presence of water vapor or after long usage. So far as we are aware, all of these observations have remained unpublished. Hahn, in the Int. Cong. f. Angewandte Chemie, Berlin, 1903 (vol. 1, p. 714), notes the devitrification of a quartz glass tube at 1100°. He also identified the crystal formation under the microscope as tridymite.

fully carried out which appear to clear up the situation, even though the inversion temperature cannot be determined with any great accuracy.

First of all, we heated a large charge of finely ground quartz and followed the temperature curve carefully from 400° to 1600°. It was found after the experiment that the quartz crystals had for the most part gone over into tridymite and the change in the volume accompanying the inversion had generated enough pressure to completely shatter the open platinum crucible which contained the charge. The change was so gradual, however, that no record of it appeared upon the thermal curve. Subsequent experiments in which we endeavored to change crystalline quartz into tridymite at lower temperatures were successful as far down as 1100°. To be sure, entire crystals showed no change whatever after six hours' exposure at 1400°, but powdered quartz is completely changed into tridymite after a few hours at that temperature. On the other hand, if finely divided amorphous silica, i. e., fused ("quartz glass"), or better, precipitated silica, be allowed to remain for a short time at any temperature above 1000°, it changes promptly to tridymite—the precipitated material very rapidly, the quartz glass much more slowly. Neither the glass nor the precipitated silica ever crystallized as quartz at temperatures above 1000°, nor is there any difference in the optical properties of the tridymite obtained at the different temperatures, either from the quartz crystals or the amorphous silica. The rate of change is much influenced by the fineness of the powder, although there is no difficulty in recrystallizing large blocks of solid quartz glass at the higher temperatures. In our experiments in the preparation of quartz glass,* we frequently obtained isolated spherulites of tridymite several millimeters in diameter, even with rapid cooling, which appeared to have been started by a grain of graphite or carborundum powder accidentally falling into the melt. On one occasion the entire block was coated with tridymite to a depth of a millimeter or more.

We have therefore succeeded, by direct experiment upon pure silica, in establishing the fact that tridymite, and not quartz, is the stable crystalline form of silica for all temperatures above 1000°.

At lower temperatures than this it is impossible, in view of the inertness of the substance, to obtain any further reaction, even with the finest precipitated silica, within the time available for a laboratory experiment. A month's exposure at 900° produced no change. We therefore followed the example of

* Day and Shepherd, "Quartz Glass," Science, xxiii, p. 670, 1906.

several distinguished predecessors in this field, and tried various catalyzers.

Formation of Quartz.—Hautefeuille thought he had produced quartz crystals by fusing amorphous silica with sodium tungstate at 900°, but the methods of high-temperature measurement commonly employed in his time were very imperfect, and the temperature is undoubtedly too high. He has also stated that he obtained it by fusion with lithium chloride. Both Hautefeuille and Margotet have recorded the fact that in the presence of lithium chloride amorphous silica changes to tridymite at high temperatures and to quartz at low temperatures. We obtained quartz crystals from glass by the use of a mixture of 80 per cent KCl with 20 per cent LiCl at all temperatures below 760°, while at temperatures of 800° and higher only tridymite crystals appeared. The same results were obtained with vanadic acid and with sodium tungstate. The inversion point

$$\text{quartz} \rightleftarrows \text{tridymite}$$

therefore occurs at about 800°. This conclusion is subject to the assumption that the inversion temperature is not lowered by the catalyzing agent—an assumption which seems to be justified by the fact that the quartz crystals obtained in this way (judged by the optical properties) appear to hold none of the reagent in solid solution.

The situation is then, briefly, this: Both quartz and amorphous silica at high temperatures change to tridymite. Quartz is consequently the unstable form of silica from 800° upward, and will go over into tridymite whenever conditions favorable to the change are present. The melting temperature of silica is therefore properly the melting temperature of tridymite and not of quartz as it is commonly described. We have once or twice succeeded, by extremely rapid heating, in melting quartz as such, or more correctly speaking, in carrying a quartz charge past the melting temperature of tridymite, melting a portion of it and finding a residue of quartz afterward which had neither inverted nor melted. It would hardly be possible by any known method, however, to obtain a separate melting temperature for quartz independently of tridymite.

The reverse operation, showing that tridymite inverts to quartz at temperatures below 760°, cannot be carried out in the laboratory without the use of catalyzers on account of the extreme slowness of the change. In the presence of the mixture of 80 per cent KCl and 20 per cent LiCl, quartz began to appear from tridymite in quantities sufficient for positive identification after an exposure of five or six days, at about 750°.

No effort was made to invert an entire charge on account of the slowness of the change and the fact that its character was now fully established. The glass crystallizes to quartz below 760° and to tridymite above 800°, crystalline quartz goes over to tridymite above 800°, and tridymite to quartz at 750°; the change is therefore enantiotropic and not monotropic.

Incidentally, a sufficient reason has been given for the complete failure of experimenters to produce quartz without catalysis. If dry silica at 900° is so inert as to undergo no reaction at all during a month's exposure under favorable conditions, how can we expect reaction below 800° where the viscosity is even greater? Silica must be crystallized below 800° to produce quartz.*

Density of Silica.—The density of the silica used and obtained in our experiments was determined with the following results, the aggregate impurity being not over one-tenth of one per cent:

Purified Natural Quartz.	Quartz Glass.	H_2O at 25° = 1.
2·655	First preparation,	2·209
2·653	" "	2·215
2·654	" "	2·212
	Second "	2·213
	" "	2·215
Mean, 2·654 (25°)		Mean, 2·213 (25°)

It will be noted that there is a difference of more than 16 per cent between the density of the glass and that of the quartz crystals.

A charge of powdered crystalline quartz heated for several days at 1200° appeared under the microscope to be homogeneous tridymite. Some observations of its density are contained in the subjoined table under the heading "tridymite from quartz."

*E. Baur (Zeitschr. f. phys. Chem. xlii, p. 575, 1903) appears to have obtained tridymite and quartz side by side from a mixture of 5^{grms} SiO_2, $4{\cdot}3^{gr}$ AlO_2Na and 12^{cc} water heated for six hours in a closed steel bomb at 520°. We find it very difficult to reconcile this result with our experience. That tridymite is not the stable phase at this temperature under the conditions of the experiment appears to be established beyond reasonable doubt by our own work, although we have never studied a mixture of exactly this composition. We should therefore not expect it to form in such a melt, certainly not in the presence of quartz. If tridymite came to be present by accident as a result of some previous operation, or by the temperature in the furnace having been too high, it might revert gradually to quartz and thus explain the presence of both forms in such a charge. Until we are in position to repeat Baur's experiment, therefore, we are unable to explain the simultaneous appearance of quartz and tridymite except by assuming that two operations have taken place: (1) a formation of tridymite, and (2) a partial reversion to quartz, or some unchanged silica may subsequently have formed a quartz at a lower temperature.

A similar charge obtained by crystallizing the glass at 1200° (three days) also showed no residual glass under the microscope. Its density is given under the heading "tridymite from glass." A second table contains confirmatory measurements upon a second preparation heated to a slightly different temperature.

Tridymite.

(H_2O at 25° = 1)

First Preparation, (1200°).		Second Preparation. (6 days at 1160°).	
From quartz.	From glass.	From quartz.*	From glass.
2·325	2·316	2·327	2·319
2·330	2·318	2·325	2·318
2·325	2·316		2·316
	2·319		
Mean, 2·326 (25°)	Mean, 2·317 (25°)	Mean, 2·326 (25°)	Mean, 2·318 (25°).

Whether the quartz had not completely changed to tridymite, or the glass was incompletely crystallized, or perhaps both, is of little moment. It is a very slow change and the agreement between the values obtained by the two methods is sufficiently good, when considered in the light of their identical optical properties, to establish the absolute identity of the tridymite formed from the glass and from the quartz crystals.

The Lime-Silica Series.—Having determined the properties of our two component minerals, we are prepared to enter upon the study of their relation to each other in mixtures of various proportions. It will be borne in mind that inasmuch as we found no proper melting-*point* for pure silica on account of the inertness (if we may so describe it) with which it resists molecular deorientation when heated, so compositions which are immediately adjacent to the silica end of the series may be expected to show the same property and to yield but little information from a direct application of the usual pyrometric methods. Similarly, pure calcium oxide and its immediate neighbors are well out of reach of accurate measurement by any existing pyrometers. But even without these important measurements, we have been able to obtain sufficient information in the more inaccessible portions of the curve to enable us to describe all the reactions involved with little probability of error. Inasmuch as lime is one of the most refractory minerals known, it will require no apology if we simply leave its thermal constants until greater perfection in pyrometric measurements shall have been attained.

Preliminary Orientation.—Given chemically pure and *well mixed* (by grinding and *repeated melting*) preparations, it is

* This preparation was afterward found to contain some unchanged quartz.

not a difficult matter to secure a preliminary survey of a field of this kind. The mineral wollastonite is known, and more than that, is known to possess a melting temperature lower than either lime or silica. There is therefore immediate reason for anticipating eutectic relations somewhere in the series. If wollastonite forms a eutectic with components on one or both sides of it, mixtures containing slightly more lime or slightly more silica than wollastonite will have lower melting temperatures than it. A simple and effective mode of preliminary procedure is therefore to take a tiny pinch of a number of the percentage mixtures adjacent to wollastonite, place them in order upon a narrow platinum ribbon which can be heated electrically to uniform brightness, and observe the order in which they melt. No temperature measurement is worth while; the information obtained can serve only for orientation and must be verified by more reliable pyrometric methods.

If a eutectic is present on either side of the compound, it will be the first to melt, and the compound last; the intermediate mixtures are not important. If the materials are not too viscous the melting will be sharp and the material will crystallize again on slow cooling. A few repetitions, or the introduction of intermediate compositions in doubtful cases, will usually enable a preliminary curve to be drawn in which the compounds and eutectics which are within reach will be correctly located. In fact, for many substances they can be very exactly located in this way. Intermediate compositions, on the other hand, may be very misleading, depending upon the behavior of the eutectic present after the melting temperature of the latter has been passed. (In applying this method, very small particles ($0{\cdot}2^{mm}$) must be used in order to obtain comparable results.)

Proceeding in this way, a eutectic will be readily located between silica and wollastonite at the composition 63 per cent SiO_2, 37 per cent CaO, and another on the other side of wollastonite at the composition 46 per cent SiO_2, 54 per cent CaO. We will allow the other component of this second eutectic to remain unidentified for the moment, as no stable lime-silica mineral richer in lime than wollastonite is known. If we continue our platinum ribbon experiment with continually increasing percentages of lime, we shall find that after one or two steps beyond this second eutectic the platinum ribbon will burn out without melting the little grains. In other words, the melting temperatures of lime-silica mixtures richer in lime than 60 per cent are all higher than that of the platinum. To meet this difficulty we built a small but very serviceable piece of apparatus the essential portion of which is a thin ribbon of pure iridium about 2^{mm} wide and 10^{cm} long, stretched between electrodes

under constant tension. Immediately beneath the ribbon and supporting its weight was a slender block of selected magnesite. The ribbon and its supports were then enclosed within concentric glass tubes between which cold water was kept flowing. The atmosphere immediately surrounding the ribbon was nitrogen.* With this ribbon we proceeded as before, laying out a whole series of compositions from 60 per cent CaO on. With

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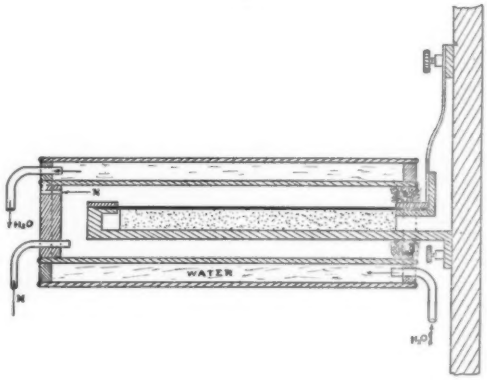

this little apparatus, of which fig. 2 will convey a fairly clear idea, we promptly discovered a third and very sharp eutectic with the composition 67 1/2 per cent CaO, 32 1/2 per cent SiO_2, and a maximum indicating a probable compound at 65 per cent CaO, 35 SiO_2, which corresponds to the anticipated orthosilicate. No other points were obtained up to 2100° C.

Thus in a very short time and in this simple and expeditious way we were able to locate three eutectics (37, 54 and 67 1/2 per cent CaO) and two compounds (48 and 65 per cent CaO) between lime and silica, canvassing for the purpose practically all the compositions from pure lime to pure silica at intervals of 1 or 2 1/2 per cent, and all temperatures from 500° to 2100° C. Beyond 75 per cent lime and below 32·5 per cent the method yields no information, for reasons which have been elaborated elsewhere. All the important determinations were verified by numerous repetitions.

If we now compare the compounds obtained by this preliminary investigation with those which we were led to anticipate from Boudouard's observations, as well as from the hypothetical

* Even with this precaution, the iridium volatilized so rapidly that the magnesite was black after *thirty minutes* heating.

silicic acids, we find that we have located two—the metasilicate and orthosilicate—and missed two—the åkermanite analogue $4CaO, 3SiO_2$, and the tricalcic silicate. The next step was therefore obviously to bring all our resources to bear upon these particular compositions in order definitely to ascertain whether such compounds can exist when the components are pure, and if so, under what conditions and with what properties.

The Åkermanite Analogue.—The åkermanite analogue ($4CaO.3SiO_2$) was first taken up and the neighboring concentrations investigated at intervals of 1 per cent with the greatest care. A large charge of this particular composition was repeatedly melted and examined under the microscope, but it failed to show homogeneous structure or any characteristic property of a compound. On the other hand, the pseudo-wollastonite and the orthosilicate appeared in the proportion appropriate to its place in the series. Furthermore, since the melting temperatures of these mixtures were within the reach of our platinum furnaces, and therefore of our most sensitive pyrometric measurements, we were able to hold the temperature constant at any desired point and then by rapid cooling (quenching in mercury) to fix any phase which might have been present and become unstable below that temperature. Here again we found that pseudo-wollastonite and the calcium orthosilicate were the only phases which could be separated from this or any mixture of the pure components in this neighborhood. It is our belief, therefore, that the åkermanite mineral cannot exist between the pure components and is only possible when other substances are present. This is further indicated by the fact that the metasilicate of calcium in the presence of magnesium forms a solid solution of which the limiting concentrations are relatively wide and which would easily account for the åkermanite mineral produced from the fusion of the three components.

The Orthosilicate of Calcium, $2CaO,SiO_2$ (65·00 per cent CaO).*—It has long been known that the orthosilicate of calcium, although not found in nature, can be formed by the fusion of the pure components. The temperature of fusion is very high and the crystalline material obtained disintegrates spontaneously at the lower temperatures The cause of the disintegration has not been carefully studied heretofore, and optical determinations of it are difficult, owning to the extreme fineness of the disintegrated product. Our investigation establishes the fact that the orthosilicate of calcium can exist in

* The metasilicate of calcium has been made the subject of a special paper by Allen, White and Wright (loc. cit.) and will not receive detailed consideration here.

three polymorphic forms in enantiotropic relation to each other, which we have designated as α, β and γ, in the order in which they form from fusion. The α-form is the only modification which is stable in contact with the melt. Its specific gravity is about 3·27, determined in methylene iodide solution upon fresh crystals. Its hardness is 5–6, Mohs's scale; crystal system, monoclinic.

Below 1410° the α-form changes into the β-form, of which the density 3·28 (measured by comparing the indices of refraction) is but little different from that of the α modification. The substance was too unstable for determinations of the density to be made in the ordinary way. It crystallizes in the orthorhombic system. The inversion point between the α and β varieties is well marked and distinguishable over almost the entire range of compositions of which the orthosilicate is a component, as indicated in the diagram (fig. 3, line MN). The inversion of β into γ occurs at about 675° with a large increase of volume which at once explains the disintegration of the material. The temperature at which this inversion occurs is somewhat variable, and it is not readily reversed. It is much too slow a change to admit of pyrometric determination, but it is possible to locate it approximately by quenching the material from selected temperatures in the neighborhood of the inversion point. The usual procedure was to take a small portion of the disintegrated material, fold it tightly between thin strips of platinum and place these in the furnace. The temperature was then raised to any chosen value and maintained constant for periods of time varying from six hours to three or four days. At temperatures far enough removed from the inversion point, the transition from one form into the other was fairly rapid, but as the temperature of inversion approaches, equilibrium is attained with increasing difficulty. After the furnace had remained at this constant temperature for a length of time, it was opened, the platinum strips containing the orthosilicate were removed and quickly plunged into mercury. In this way, from temperatures just above the inversion point, it was possible to fix the β-form long enough to allow of its optical determination.

The disintegration on cooling appeared to depend considerably upon whether or not the α-form had first been allowed to change into the β-form. For example, if a small portion of the orthosilicate is fused before the oxyhydrogen blast and then plunged directly from the flame into mercury, the quenched material will usually be stable for a considerable time. If the flame is removed but a moment and the slightly

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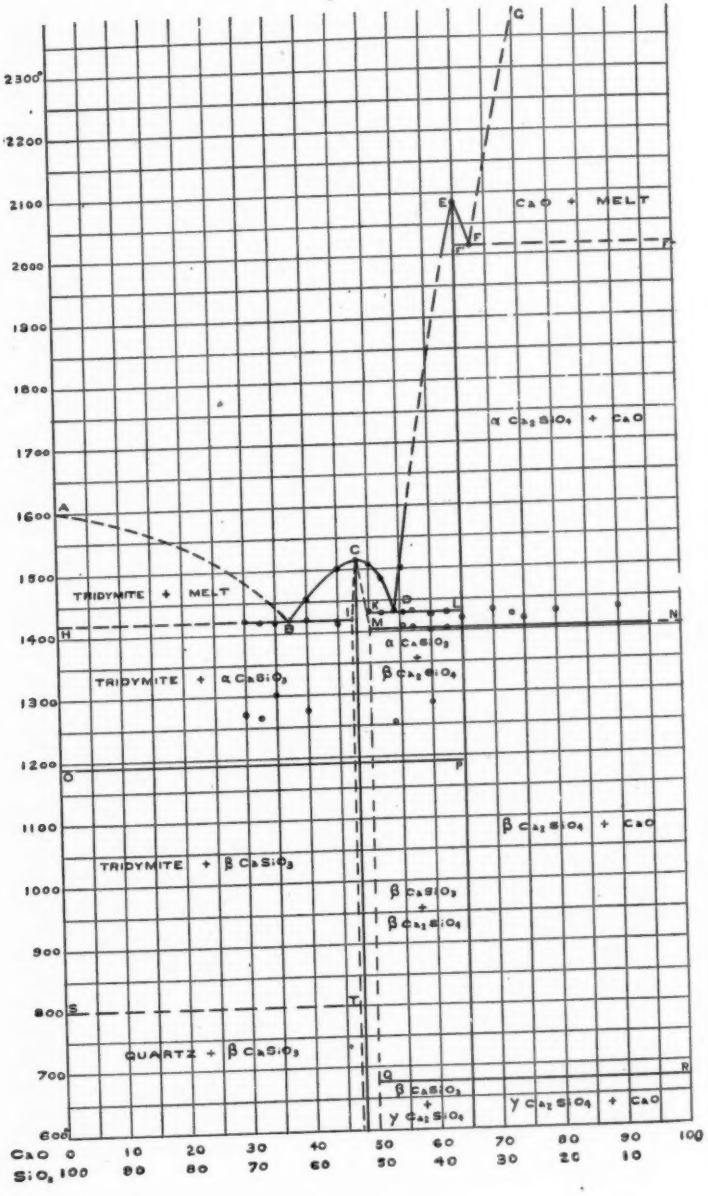
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R
S
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CaO + MELT
α Ca2SiO4 + CaO
TRIDYMITE + MELT
α CaSiO3 + β Ca2SiO4
TRIDYMITE + α CaSiO3
β Ca2SiO4 + CaO
TRIDYMITE + β CaSiO3
β CaSiO3 + β Ca2SiO4
QUARTZ + β CaSiO3
β CaSiO3 + γ Ca2SiO4
γ Ca2SiO4 + CaO
CaO 0 10 20 30 40 50 60 70 80 90 100
SiO2 100 90 80 70 60 50 40 30 20 10

cooled specimen plunged from white heat into mercury, disintegration is immediate. This phenomenon was further verified by fusing the material and dropping it into a furnace held at about 1200° C. After a few moments the charge was then removed and quickly plunged into mercury. Treated in this way, all of α goes over into β, which in turn will disintegrate completely with little or no delay after reaching the $\beta \rightleftharpoons \gamma$ inversion temperature. One will sometimes get the α-form by slow cooling, but never the β-form.

The γ-form of the orthosilicate crystallizes in the monoclinic system. Its density, determined in turpentine, by the picnometer method, is

2·973
2·975

Mean, 2·974

The difference in volume between the γ and α or β forms is therefore nearly 10 per cent, and since the α and particularly the β-form goes over into the γ at low temperatures with the greatest readiness, the disintegration of the fused orthosilicate is readily explained.

Neighboring mixtures containing the orthosilicate as a component disintegrate beginning with compositions containing only 51 per cent of lime. The disintegration of this preparation is, however, very slow, and usually does not take place at all unless the mixture has been held for some time at a relatively high temperature. The 54 per cent mixture can also be readily obtained without disintegration, but with more than 54 per cent of CaO, disintegration always occurs under the ordinary conditions of preparation.

If the orthosilicate be heated to temperatures only slightly above QR (fig. 3) so as to produce the β-form without sintering, disintegration does not appear on cooling for the reason that the change in volume is not apparent in the powdered material. If the charge be heated to about 1400°, or above 1410° where the α modification appears, it sinters tightly together and the disintegration phenomenon is again observed. Charges sintered together at 1400° to 1500° and held continuously at any temperature above QR do not disintegrate so long as this temperature is maintained, but as soon as the temperature drops below QR, disintegration recurs, but not at a constant temperature nor at any characteristic rate, the change being very dependent upon the conditions obtaining at the time.

The orthosilicate is easily attacked by water, giving an alkaline reaction, even when the water is cold, while with boiling water

it is possible to wash out as much as 10 per cent of lime. This probably accounts for the absence of this mineral in nature. Ammonium chloride solution even when cold decomposes all the mixtures of CaO and SiO_2.

The tricalcic silicate, $3CaOSiO_2$. — This silicate owes its supposed existence mainly to those investigators who have found it necessary to postulate such a compound in order to explain the constitution of portland cement. So far as the literature shows, no one has ever isolated and described a pure and homogeneous compound of this composition or defined its properties.* Many and varied attempts to make it have uniformly resulted in mixtures in which poor optical properties have made the conclusions insufficiently positive.†

We began the investigation of this composition by fusing the components in the proper proportions and examining the fused product microscopically as others had done. Most previous investigators, however, appear to have depended for microscopic evidence upon the ordinary optical figures and interference colors. Now, it so happens that this mixture when fused crystallizes in an extremely fine structure in which the interference colors are quite different from those of the orthosilicate to be sure, but this is merely the result of the fine state of division and the overlapping of the crystals, and not to another compound. If one examines any of the compositions in which the tricalcic silicate might be expected to figure, using the very sensitive index of refraction as a test of homogeneity, he will find that in every preparation containing more lime than 65 per cent (orthosilicate composition), there is an excess of free lime which can be positively identified. We have fused the tricalcic silicate composition, cooled it rapidly and slowly in various ways, without once failing to find free CaO present in quantity. Through the kindness of Dr. Clifford Richardson we were also given an opportunity to examine some of the tricalcic silicate prepared and described by him, and while its

*It is sometimes described as "nearly homogeneous."

†A moment's consideration should suggest that there is no real necessity for assuming the existence of the tricalcic silicate in order to explain the nature of portland cement. It is at least a three-component system with a great number of possibilities. The real difficulty appears to have been that crystallized lime is relatively inert and does not readily give the reactions common to ordinary lime, consequently the tests which were thought to demonstrate the absence of free lime in these preparations have proved very misleading. For example, we have found that crystals of CaO are but very slowly attacked by water (see p. 271). Another argument which is freely offered—that there can be no free lime present "because if free lime is added the cement dusts spontaneously," is obvious fallacy. Free lime does not cause the dusting and if it did the fact that the *addition* of free lime caused dusting would be no proof that none was present. (Cf. 52 per cent CaO, 48 SiO_2.)

ordinary appearance under the microscope differed from that of the orthosilicate, a study of the index of refraction showed the supposed tricalcic silicate to be a mixture of the orthosilicate with free lime. Having failed to obtain a single tricalcic silicate which did not contain free lime, and because every specimen which we examined, including many which had been prepared by others, also showed the orthosilicate to be present, we were forced to conclude that the tricalcic silicate has no real existence. We also tried fusing the tricalcic silicate composition with a flux, but the product was always the orthosilicate of calcium with free lime.

Although we are anticipating pyrometric studies which follow, a single glance at our diagram, fig. 3, will show that we have found and measured the $\beta \rightleftarrows a$ inversion of the orthosilicate in all the compositions up to 90 per cent lime, which we could never have done with a tricalcic silicate intervening unless the tricalcic silicate be assumed to possess an identical inversion,—which would be rare coincidence. We have, therefore, complete optical and pyrometric evidence of the persistence of the orthosilicate throughout the supposed tricalcic silicate region, and no compound of tricalcic silicate composition can exist there.

By way of completing the search for hypothetical compounds, we also examined compositions corresponding to the trisilicic acid, but found that the mixtures of lime and silica from which the salt of this acid might be expected to crystallize did not give any new phases. These mixtures showed well developed pseudo-wollastonite with the tridymite eutectic, and neither rapid cooling nor crystallization of the glass at low temperatures gave any indication whatsoever of the hypothetical compound.

Thermal Apparatus.—The thermal measurements to be detailed in the pages which follow were obtained for the most part in furnaces and by methods which have been described in sufficient detail elsewhere.* The work which has been done with the apparatus since that time has exposed one weakness which will be given detailed consideration at a more appropriate time and place, but will be outlined here for the use of others who may have occasion to employ this extremely useful and accurate apparatus. For certain reasons of convenience rather than of necessity, the platinum coils which we have heretofore employed for heating purposes have usually contained 10 per cent of iridium. It has now been found that even in a nitrogen atmosphere this iridium sublimes slowly at temperatures above 1200° and enters and contaminates the wires of the thermoelement, if they are exposed, even in the

*Day and Allen, *loc. cit.*

colder parts of the furnace. Unglazed porcelain offers no protection against this iridium. The effect of this contamination is to make the thermoelements read too low. The error is noticeable after a single hour's exposure (perhaps 1/2°), and will gradually increase to fifty degrees or more in a few weeks of continuous usage, the amount depending considerably upon the temperatures employed. The remedy is simple and sure,—*use no iridium in the furnace.* An element once contaminated in this way can only be restored by cutting off the exposed portion.

Above 1600° the platinum coil and the thermoelement gave place to the iridium tube furnace and the Holborn-Kurlbaum optical pyrometer. The adjoining diagram (fig 4) contains

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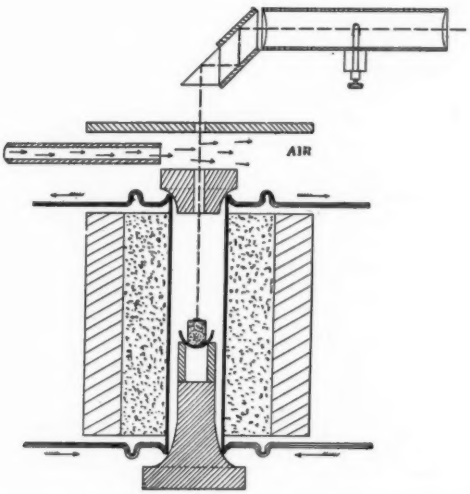


sufficient details to show almost at a glance the operation of the system. A straight iridium tube about 18^{cm} long and 4^{cm} in diameter is fed by an alternating current of low voltage, led in through platinum and silver flanges at the ends. Fused magnesia serves as insulating material and a base of magnesia supports a small iridium crucible in the position indicated. A small opening in the magnesia cover enables the pyrometer to be sighted on any point within.* The furnace will reach temperatures of 2100° C. and is almost indispensable at very high temperatures where an oxidizing atmosphere is important.

*This furnace was made for us by Dr. Heraeus of Hanau, Germany, to whom, as well as to his associate, Dr. Küch, we are indebted for many courtesies.

The Holborn-Kurlbaum pyrometer is a very simple telescope consisting of two cheap lenses, in the focus of the first of which (eye-piece) is placed a small incandescent lamp in which the current and therefore the brightness of the filament can be varied. The operation of measuring then consists merely in focussing the telescope upon the hot body of which the temperature is required and changing the current in the filament until the latter can no longer be seen against the hot object observed. The current then passing through the filament is a measure of the temperature. Monochromatic light (preferably red) only is used. The calibration of this instrument is arbitrary. It requires merely to be directed at a hot object of which the temperature is known, and the current observed. The relation between current and temperature for several temperatures can then be elaborated into a curve for purposes of interpolation or extrapolation. One condition must not be overlooked in the use of such an instrument,—the radiant energy sent out at a particular temperature is different for different substances unless they are enclosed within a hollow body of uniform temperature, in which case all bodies radiate alike and perfectly. Such a hollow body with a small opening has been called by Kirchhoff a "black body" or perfect radiator, and the radiant energy passing through the opening, black radiation. A fair working test for the "blackness" of radiation within a furnace, for example, is obtained by observing whether objects within can be distinguished. When all detail disappears within a furnace, its radiation is reasonably black. This is approximately true at the center of nearly all enclosed electrical resistance furnaces in which no combustion is going on, but if the temperature is high it is usually not entirely uniform even for small areas, and the radiation is consequently not black.

For purposes of comparing the thermal constants of different substances of unknown radiating power, therefore, we first obtained small incandescent lamps which had been calibrated upon a black body at the Reichsanstalt and verified the calibration upon a similar body in our own laboratory for the purpose of comparing standards. We did not deem it safe to assume the approximate blackness of charges within the furnace, although the conditions sometimes appeared sufficiently good to warrant it. We took two trustworthy fixed points, the melting temperature of anorthite (1532°) and platinum (1720°), both being in the region in which we proposed to apply the method, and observed the radiation from a tiny fragment of iridium ribbon at those temperatures. In this way we obtained two points slightly below the black body curve and passed through these an empirical curve parallel to

the standard curve. Our temperatures were measured in terms of this empirical curve. Since differences of less than five degrees can hardly be distinguished by this apparatus at such high temperatures, the assumption here made that the radiation from iridium is of uniform quality throughout the region between 1600° and 2100°, will hardly be called in question. After the temperature scale was established in this way the iridium fragment was laid on the top of each charge during the measurement and all determinations were made in terms of the radiation from it.

With this pyrometric apparatus we undertook to examine all the mixtures within reach from lime to silica which the microscopic study had shown to be important. The mixtures were first examined in charges of 100 grams between 500° and 1600° in a furnace of the type described by Day and Allen (*loc. cit.*), supplemented where necessary by observations at higher temperatures in the iridium furnace with the optical pyrometer. The relative sensitiveness of the two methods is roughly one to ten, i. e., the smallest temperature changes which the optical pyrometer can detect are fully ten times as great as those which can be readily measured with the thermoelement. Furthermore, the optical pyrometer is merely a device for estimating temperatures by observation from without the furnace. It enables an observer to heat a charge to a certain temperature but not to tell whether anything takes place there except by removing the charge from the furnace for examination. It is not adapted to the determination of thermal constants by direct observation except in the case of the melting temperature of pure compounds or eutectic mixtures which melt sharply into a thin liquid.

It has been our universal experience that changes of state which are subject to lag are much more easily and certainly determined from heating than from cooling curves. Undercooling in these ultra-viscous media cannot be prevented with certainty by any of the usual methods. Superheating is also unavoidable at times, as we have already noted in the case of quartz and elsewhere. In these cases the change of state required by conventional definitions simply cannot be determined as a point. Where the inertness is not so great as to be prohibitive of all measurement, our uniform experience has been that the melting temperature can often be established with confidence, where solidifying temperatures cannot. Similarly, inversions in the solid state can usually be fixed upon a curve of rising temperatures with greater certainty than upon a cooling curve.

The temperature constants.—We have now definitely located the compounds of lime and silica which can exist between the

pure components together with the eutectics which they form. It only remains to study their thermal properties somewhat more consistently with the help of the apparatus which has been described. It was not found possible to determine the presence of the eutectic (Line HBI, fig. 3) in the 10 and 20 per cent compositions, for reasons which will have become sufficiently clear already, but the microscopic evidence shows the tridymite to be normal, whether it forms from pure silica or in the presence of lime, so that the eutectic must extend over to the silica axis. From 30 per cent on there was no difficulty in observing it pyrometrically. The observations are included in Table I.

TABLE I.

	Eutectic.	*Tridymite + Pseudo-wollastonite.* (Line H I, fig. 3.)			
Percentage of CaO.	30	32	35	40	45
Eutectic melts	1420°	1417°	1120°	1421°	1419°
		1419	1423	1420	1419
			1414	1422	1406
			1416	1420	1406
Mean	1420°	1418°	1418°	1421°	1413°

The liquidus AB (fig. 3) has been drawn as a dotted line. The value assumed for the melting temperature of silica is based upon considerations which have been elaborated elsewhere (p. 272). It requires no further comment except perhaps to call attention to the fact that it is much lower than the temperature usually assigned to it. As the mixtures grow richer in lime, the melting of the excess of silica seems to be considerably facilitated, but there are no points sufficiently sharp to serve any purpose as quantitative determinations until we reach the composition $30CaO, 70SiO_2$. The microscopic evidence is however both satisfactory and sufficient as to the nature and continuity of the curve.

Along the branch BC (fig. 3) of the liquidus, the pseudo-wollastonite is the solid phase. It crystallizes from these mixtures in laths between which an extremely fine-grained, almost sub-microscopic eutectic appears.

It may be remarked in passing that the "eutectic structure" in minerals is by no means so characteristic as in the case of the alloys. Owing to the great viscosity of these melts and consequent slowness of diffusion, it is evident that there is no opportunity for the formation of the characteristic grain structure which we have come to associate with the eutectics of alloys. This almost complete absence of diffusion in silicate melts makes it necessary to proceed with great caution in applying to minerals the methods which are easily and effectively applied to the alloys. For example, in alloys it is possible to crystallize out a portion

of the solid phase, then to separate the mother liquor and, by analysis of the two, to determine the composition of the solid phase. In the case of mineral mixtures, the segregation of the eutectic is, for laboratory experiments at least, very indefinite. We have repeatedly examined different regions of a charge in which the eutectic was known to separate, in the hope of finding it segregated towards the middle of the charge, as commonly happens with alloys, but in no case were we able to detect more of the eutectic in one part of the charge than in another. It is usually finely divided and intimately mixed with the primary crystals.

The properties of the pseudo-wollastonite which separates along the branch BC are not quite identical with those of the compound when prepared pure, from which it is evident that a certain amount of silica must be taken up by it in solid solution. The amount thus held in solution is certainly less than 2 per cent, but its exact determination microscopically is very difficult indeed. Furthermore, this pseudo-wollastonite when changed to wollastonite still shows a slightly different optical character from the pure material, showing that the solid solution apparently continues after the inversion. For brevity, the pseudo-wollastonite has been designated α-$CaSiO_3$, and wollastonite β-$CaSiO_3$ in fig. 3. The branch of the liquidus CD was readily determined, as well as the beginning of the branch DE. It was not possible, however, to follow the branch DE beyond 57 per cent owing to the steepness of the curve, which rapidly carries it out of the range of the accurate thermoelectric methods.

TABLE II.

Curve of Melting Points.

(Curve A B C D E F G, fig. 3.)

Percentage of CaO	40·0	45·0	48·2	50·0	52	54	55·5	65	67·5
Component in excess melts	1457°	1504°	1512°*	1505°	1484°	1435°	1516°	2077°	2015°
	1457	1504		1510	1483	1437	1489	2085	
	1445	1497		1509	1485	1434		2083	
		1494			1484	1435			
					1483	1435			
					1482	1432			
					1488	1432			
						1435			
						1433			
						1430			
						1429			
Mean	1453°	1500°	1512°*	1508°	1484°	1433°	1503°	2082°†	2015°†

* Determined by Allen and White (*loc. cit.*).

† Determined with the Holborn-Kurlbaum optical pyrometer in the iridium furnace.

Observations along the curve of melting points are contained in Table II. The eutectic KL (pseudo-wollastonite + *a*-calcium orthosilicate, Table 3) was found in all compositions containing more than 50 per cent and less than 65 per cent CaO. Not a trace of it could be detected in the 65 per cent composition, though diligent search was made for it. A great many determinations were made of it of which the values are given in Table III.

TABLE III.

Eutectic. Pseudo-Wollastonite + a-Calcium Orthosilicate.

(Line KL, fig. 3.)

Percentage of CaO	50	52	54	55·5	57	60	62·5
Eutectic melts	1428°	1432°	1435°	1427°	1419°	1431°	1426°
	1435	1428	1437	1428	1428	1422	1431
	1432	1428	1434	1427	1428	1425	1429
		1428	1435	1428	1430	1426	
		1429	1435	1427	1429	1426	
		1428	1432	1428	1429	1426	
		1430	1432	1429	1433		
		1433	1435	1431	1434		
		1426	1433	1430	1434		
		1433	1430	1430	1441		
		1427	1429		1438		
		1431			1435		
		1430					
		1426					
		1430					
		1431					
Mean	1432°	1430°	1433°	1429°	1431°	1426°	1429°

The properties of the metasilicate separating along CD are also slightly different from those of the pure pseudo-wollastonite, and up to 50 per cent the mixture appears homogeneous, so that the metasilicate probably takes up about 1 per cent of orthosilicate in solid solution. The melting point of the orthosilicate determined in the iridium furnace was found to be

	2077°
	2085°
	2083°
Mean	2082°

Another charge observed at 2035° was found entirely unmelted. Optical methods of temperature measurement are not competent to determine the melting temperature of the

orthosilicate in the presence of the eutectic for reasons already explained (p. 267), but the eutectic or the compound is readily measured by itself once the composition has been determined. Applying the method to the 67½ per cent mixture, therefore, it was found to melt very sharply at 2015°. Neither the orthosilicate nor the 70 per cent CaO composition showed any trace of fusion at this temperature. Since the microscopic properties of the orthosilicate remain unchanged in the presence of an excess of lime or of silica, it follows that the orthosilicate does not form solid solutions with either lime or silica. Both eutectics will therefore continue up to the orthosilicate. Above the lime-orthosilicate eutectic the pyrometer affords no further information regarding the melting point curve.

The line MN (fig. 3) represents the temperature at which the inversion to β-orthosilicate occurs. It will be noted that the inversion is frequently delayed by superheating, especially in the region remote from the eutectic, but it was always possible to show by quenching the material from above and below these temperatures that the variation is merely due to the inevitable lag of the reaction. Between 50 and 65 per cent of lime, the two heat changes at MN and KL lie so close together that it was very difficult to separate them. The pyrometer shows two points plainly, but each is somewhat influenced by the presence of the other. We were able, however, to distinguish them beyond possibility of confusion by holding the furnace constant at 1425° and quenching the charge in water. These conditions yield α-orthosilicate + pseudo-wollastonite, while if the temperature is held at 1390–1400°, β-orthosilicate + pseudo-wollastonite results. The inversion temperatures are contained in Table IV. Mean values lose much of their significance in determinations of inversion temperatures where superheating can occur and are accordingly omitted from the table.

TABLE IV.

Inversion β-Orthosilicate to α-Orthosilicate.

Percentage of CaO	55·5	57·0	60·0	62·5	65·0	70	73	75	80	90
Inversion	407°	1395°	1404°	1396°	1426°	1409°	1426°	1415°	1407°	1433
tempera-	1414	1412	1411	1397	1421	1405	1425	1421	1429	1432
ture.	1403	1419	1411	1405	1415	1412			1432	1433
	1411	1415	1398	1398	1414				1425	
		1406	1402	1408	1412					
		1406	1404	1407	1413					
		1404	1405	1401	1417					
			1388		1423					
					1411					

The scattered points lying below 1300° (fig. 3) occur only in the compositions in which the metasilicate is present, and correspond, as a microscopic examination at once shows, to the change from wollastonite to the pseudo-hexagonal form. With falling temperature, the points occur very much lower or are lost, since the inversion does not occur quite as readily on cooling. Allen and White observed that this inversion could be brought about only with great difficulty with the pure metasilicate, but in the presence of an excess of either lime or silica, we found it to occur with comparative readiness (Table V) in many compositions.

The line QR is the temperature at which the reaction β into α takes place. As observed in the discussion of the properties of the orthosilicate, this reaction does not occur promptly, but is liable to very serious superheating or undercooling.

TABLE V.

Inversion β-Metasilicate to α-Metasilicate.

Percentage CaO	30	32·5	35	40	45	57
Temperature of inversion.	1273°	1274° 1263	1257° 1399 1323 1328	1288° 1266	1254°	1286°

Part III. Optical Study.

The different members of the lime-silica series are well characterized optically and can generally be distinguished under the microscope without difficulty. Occasionally, however, the preparations are extremely fine-grained and require repeated examination before the minute details of each substance in the product are fully appreciated. In actual practice, experience has shown that the best results can be obtained by examining the preparations in powdered form rather than in thin sections cut from larger fragments. The chief advantage of thin sections over the powdered material is a textural one, since by breaking any given preparation into small particles its original texture is practically destroyed. Although problems of textural differences in artificial products are not to be disregarded, actual determinations can best be made with the powder, since with it the crystallites can usually be examined separately and the optical phenomena of a single individual observed rather than those of an aggregate of overlapping and interlacing crystals, as is often the case in slides; furthermore, by embedding the fine grains in a viscous liquid, such as Canada balsam, they can be rolled about in the liquid and their optic properties in any desired direction ascertained; the refractive indices of a substance can also be determined directly

on powdered particles by Schroeder van der Kolk's method of refractive liquids and numerical constants thus obtained on grains measuring even less than ·001^{mm} in linear dimensions.

Optically, four different compounds were recognized in the lime silica series; three of these appeared in different polymorphic modifications according to the conditions of formation. Pure silica crystallized either as quartz or tridymite; calcium metasilicate ($CaSiO_3$) either as wollastonite* or pseudowollastonite; calcium orthosilicate (Ca_2SiO_4) in three forms, α, β, and γ; and calcium oxide only in one form, so far as known. The experiments indicate that for each compound the different modifications bear enantiotropic relations to one another.

Calcium oxide.—Well-developed crystals of this substance are rare and were observed only in preparations from large melts in the furnace. In intermediate mixtures between the oxide and the orthosilicate it occurs usually as small rounded colorless grains which are easily recognized under the microscope by their high refractive index and isotropism. The crystals are colorless to pale yellow, transparent, and crystallize in unmodified cubes of the isometric system. Their hardness is between 3 and 4. Attempts were made to etch these crystals by immersing them in water, but the etch figures obtained were not sufficiently distinct to be of value. They pass rapidly into Aetzhügel which cover the entire etched face. The crystals cleave perfectly after the cube (100). Their refractive index, 1·82, was determined by immersing fragments in a high refractive liquid solution of arsenic sulphide in arsenic bromide. Owing to rapid superficial decomposition, the crystals soon became coated with a thin crust which tends to decrease the accuracy of this determination of the refractive index. Optical anomalies were observed occasionally, and were due probably to internal strains. On exposure to air and moisture, the crystals slowly become hydrated and disintegrate.

The orthosilicate.—The microscopic examination of the various preparations of this compound revealed the existence of three distinct forms, α, β, and γ, which are stable over different temperature ranges. The optical properties of the α and β forms are similar and their microscopic discrimination is a difficult problem, while the γ-form, which is stable for emperatures below 675°, differs considerably from the α and forms and can be recognized with ease.

(a) *The α-form* is stable only at temperatures above 1410° and on cooling has a strong tendency to invert to the β and γ forms. It was found by experiment that if chilled very

* Compare this Journal, xxi, 89–108, 1906.

rapidly, this change could be checked, in part at least, for a considerable period of time. The *a*-form belongs either to the monoclinic or triclinic crystal system, probably the former, and shows prismatic development, with good cleavage after a face in that zone. The crystals are transparent and colorless and occur as fine aggregates so intricately intergrown that the precise determination of their optic properties is practically impossible. Twinning is a characteristic feature of this form, and is often extremely complicated. Different sets of the twinning lamellae cut each other at various angles and the sections then resemble plates of microcline or leucite. Extinction angles measured along the prism axis were noted as high as $c : a = 18°$, although smaller angles appear more frequently. The hardness is between 5 and 6. The refractive indices were measured by the method of refractive liquids: $\alpha = 1{\cdot}714 \pm {\cdot}003$; $\beta = 1{\cdot}720 \pm {\cdot}004$; $\gamma = 1{\cdot}737 \pm {\cdot}003$. Birefringence about ·02. The optical character is positive; $2V = 81°$; $2E > 180°$. This optic axial angle was measured on a section nearly perpendicular to an optic axis by the graphical method recently described by Becke.* The method is founded on the difference in curvature of the dark hyperbolic bar which passes through the optic axis, for different axial angles in the diagonal position. In place of the revolving drawing table of Becke, a different type of instrument which can be clamped directly to the microscope was used in this laboratory with satisfactory results. This method is only an approximate one and the figures obtained by its use may vary considerably from the actual values, a condition recognized by Becke himself in the original paper. The plane of the optic axes is about parallel to the direction of elongation of the crystals.

(b) *The crystallites of the β-form* are stable between 675° and 1410°; they are also prismatic in shape and show good cleavage parallel to the prism axis. They are colorless and transparent, and are orthorhombic in crystal system. Their hardness and density could not be determined directly, as this form, at low temperatures, inverts rapidly to the γ-form and can furthermore be obtained only in powdered condition. The least ellipsoidal axis c is parallel to the *c* crystallographic axis and the plane of optic axes lies in the direction of elongation of the crystals. The optic axial angle is very large. The refractive indices, $\alpha = 1{\cdot}722 \pm {\cdot}003$ and $\gamma = 1{\cdot}733 \pm {\cdot}003$, were determined by the method of refractive liquids. The birefringence is not strong, about ·01. The β-form is distinguished from the preceding *a*-form most readily by the absence of twinning and by its parallel extinction. The pro-

* F. Becke, Tscherm. Min. u. pet. Mitth. xxiv, 1905.

gressive paramorphic change of this form into the γ-form can be followed under the microscope and is interesting to watch. Shortly after cooling, irregular interference colors appear, as though induced by internal strains, and soon the mass resembles a crystalline aggregate of minute fibers. Toward the end of the process, the larger masses usually disintegrate as fine powder owing to the enormous increase in volume (about 10 per cent) during the inversion.

(c) *The γ-form* is stable at low temperatures and into it the preceding forms usually pass on cooling to ordinary temperatures. It is noteworthy that the properties of this form are unlike those of the above, particularly in specific gravity and refractive index. The density of the α and β forms is about 3·27, while that of the α-form is only 2·97. As a result, on paramorphic change in the solid state a great increase in volume takes place which at once shatters the larger fragments of the original material and causes the preparation to "dust." The γ-form can be had, therefore, only in the form of powder. It is prismatic in habit, cleaves well parallel to the long direction, is colorless and transparent, and occasionally shows indications of twinning with small extinction angles; $c : c = 3°$ was measured in one instance. The form is probably, therefore, monoclinic in system. The twinning is recognized only rarely, and the extinction usually appears parallel. The refractive indices were determined by the method of refractive liquids: $\alpha = 1{\cdot}640 \pm {\cdot}003$, $\beta = 1{\cdot}645 \pm {\cdot}003$, $\gamma = 1{\cdot}654 \pm {\cdot}003$. The birefringence is weak, about ·014; biaxial with an optic axial angle in air $2E = 52°$, measured by the graphical method of Becke on a section nearly normal to an optic axis; optical character negative; plane of optic axes perpendicular to the prism axis in contradistinction to the α and β forms. Compared with the α and β forms this form is readily distinguished by its lower refractive index, its optical character, optic axial angle, and position of the plane of optic axes to the prism axis.

The metasilicate occurs in two enantiotropic modifications, one of which corresponds to the mineral wollastonite. The second form has been called pseudo-wollastonite, and is stable above 1200°. Both these forms have been discussed so thoroughly in a preceding paper* that repetition here is unnecessary. The properties of the artificial wollastonite counterpart those of the mineral, while the pseudo-wollastonite is pseudo-hexagonal, probably monoclinic in crystal system. It is optically positive and nearly uniaxial; its refractive indices, $\alpha =$

* Loc. cit.

1·615 $\gamma = 1·636$; its birefringence is strong and considerably higher than in wollastonite.

Silicon dioxide.—In nature this oxide occurs in at least two modifications, quartz and tridymite, both of which were produced artificially in this laboratory. As a result of the experiments, the fact is well established that quartz is the stable form below about 800° and tridymite over the range 800° to the melting temperature 1600°; that, on heating, the inversion of quartz into tridymite is so extremely sluggish that quartz crystals may be heated 700° or 800° above the inversion point without changing. Quartz glass, however, can be made to crystallize to tridymite as low as 1000°.

The microscopic examination of the different artificial preparations of tridymite and quartz proved satisfactorily their identity with the natural minerals. By using the method of refractive liquids it was found possible to discriminate between quartz, tridymite and amorphous quartz with ease, even though many of the preparations were cryptocrystalline and scarcely determinable by other ordinary methods. The refractive index of amorphous quartz, obtained by precipitating silica from solution, was measured by the immersion method at 1·459±·003; later the same constant was determined more accurately on a polished face of quartz glass* on an Abbe total refractometer in sodium light with the result, 1·460.

(a) *Quartz.*—The best crystals of quartz were obtained as a byproduct from a mixture of magnesium-ammonium chloride, sodium metasilicate and water heated for 3 days in a steel bomb at 400–450°. This mixture was used by Dr. E. T. Allen of this laboratory to synthesize one of the polymorphic forms of magnesium metasilicate and to procure measurable crystals of the same. The quartz crystals thus procured were colorless, water clear, doubly terminated and well developed crystallographically. The larger crystals attained a maximum length of 2^{mm}, but were usually coated with a thin film of foreign matter and were less suited to goniometric measurement than smaller ones. The crystals are often barrel-shaped with short rhombohedral terminal faces which pass by oscillatory development into steeper rhombohedrons and finally into the prism which shows the characteristic striae of the mineral quartz. In a few of the crystals, the positive rhombohedron only was developed and the crystals were terminated by its three faces above. Several crystals were measured on the two-circled goniometer and the forms $(10\bar{1}0)$ $(10\bar{2}0)$ $(10\bar{1}1)$ observed. Other forms were noted but gave indistinct and multiple reflection signals and are not listed in consequence.

* Obtained by fusing quartz in the electric furnace under pressure.

The angle between the prism faces and the rhombohedrons $(10\bar{1}0 : 10\bar{1}1)$ measured 37° 48′ and differs appreciably from that of pure quartz, which is given by Dana, 38° 13′. The three rhombohedron faces from which this angle was obtained gave perfectly sharp reflection signals, and although the observations on the goniometer were made with the reducing attachment, the difference no doubt exists and is due probably to a solid solution of quartz with some other ingredient of the original mixture. The hardness of the crystals is 7; their specific gravity, 2·650 determined in Thoulet solution, and their refractive indices $\epsilon = 1{\cdot}654 \pm {\cdot}002$, to $\omega = 1{\cdot}644 \pm {\cdot}002$; measured by the method of refractive liquids, their birefringence is about ·01. The crystals are unaxial and optically positive, and extinguish parallel to the prism edge, which was found to be the direction of the least ellipsoidal axis c.

Quartz could not be produced by direct crystallization from silica glass, since at low temperatures at which it is stable the viscosity of the glass is too great to allow sufficient molecular mobility for the rearrangement. Fluxes or solutions were therefore used to increase this mobility, and with satisfactory results. Quartz crystallites were formed at temperatures below 760° and tridymite above that point in the same flux.

The chief effect of such crystallizing fluxes or crystallizers seems to be that they tend to increase the molecular mobility of the crystallizing material and thus procure greater freedom and power for crystallization. In many experiments performed in this laboratory it has been noted that crystals obtained directly from silicate melts are usually minute and ill-formed; while the addition of a few per cent of a second substance improves both size and quality of the crystals to a remarkable degree, even though the added substance may solidify as glass and enter apparently in no wise into the composition of the crystals.

(b) *Tridymite.*—In the experiments, well developed crystals of tridymite of sufficient size for goniometric measurements were not obtained, and optical properties alone were relied upon for its identification. The refractive index γ was measured $1{\cdot}485 \pm {\cdot}003$ on one preparation and $1{\cdot}483 \pm {\cdot}003$ on a second by the method of refractive liquids. These values are slightly higher than that given for natural tridymite, which is 1·478. No reason has yet been suggested to explain this discrepancy. The birefringence is extremely low, apparently not over ·002. The crystallites are biaxial with an optical axial angle so large and indistinct that the optical character could not be determined satisfactorily. In some of the crystals an elongation in a direction diagonal to the positions of extinction was noticeable. The best preparations of tridy-

mite were obtained by allowing large melts of quartz glass to cool slowly. On the surface of these melts radial spherulites of tridymite frequently formed and in one instance coated the entire charge with a film 1^{mm} thick of crystalline material. The preparations, however, were without exception fine-grained and so intricately intergrown and affected by optical anomalies that the exact determination of its optical constants is not possible. The same conditions obtain in the mineral tridymite and appear to be characteristic of this phase of silicon dioxide.

Intermediate mixtures.—The preparations from mixtures between pure silica and wollastonite varied greatly in texture and, with the exception of those mixtures which approached the metasilicate in composition, were found to be inhomogeneous and to consist of tridymite and one of the forms of the metasilicate. In products with less than . per cent of calcium oxide,—the eutectic composition of silica and calcium metasilicate—crystallites of tridymite were observed, often arranged in systems of lines intersecting at 90°, 60° and less angles or in rosettes and radial spherulites. The rosettes are finer grained than the crystallites and frequently appear as mere dust particles. The metasilicate is also fine-grained, without crystal outline, and includes the larger phenocrysts of tridymite. It can be distinguished from the latter most readily by its higher refractive index and stronger birefringence. The eutectic itself is extremely fine-grained and tridymite occurs then only in minute dust-like particles without discernible crystal outline.

Preparations ranging in composition between the eutectic and the metasilicate contain large, clear, lath-shaped crystallites of the metasilicate, often in parallel orientation and interrupted by a finely crystalline, less clear mixture of tridymite and the metasilicate. The optical properties of the metasilicate in these intermediate products differ slightly from those of the pure mineral, a condition which is due undoubtedly to the presence of silicon dioxide taken up in solid solution by the metasilicate. In these products the form equivalent to the mineral wollastonite was found to differ from true wollastonite chiefly in its lower refractive index and smaller optic axial angle; a measured in one instance 1·485 instead of 1·521, the a of pure wollastonite. The smallest value for the optic axial angle in air was found to be about 30° in air in place of the 70° of pure wollastonite.

The second form of the metasilicate corresponding to pseudo-wollastonite showed similar variations; its refractive indices were also lower, $a = 1{\cdot}490$ having been measured in one instance, a value ·025 lower than a for pure pseudo-wol-

lastonite. The optic axial angle was found to increase and reached a maximum of about 25° in air, whereas pure pseudo-wollastonite is nearly uniaxial. In many of the preparations hexagonal outlines of this phase are noticeable, and two sets of imperfect cleavage lines intersecting at an angle of 120° can then be seen on sections normal to the acute positive bisectrix. Mixtures containing over 45 per cent of calcium oxide appear homogeneous, and the crystals from the preparations show a continuous variation in their optic properties from that point on as the composition of the metasilicate is approached.

The microscopic study of the preparations ranging in composition between calcium metasilicate and calcium orthosilicate showed that the metasilicate is capable of absorbing a considerable amount of the orthosilicate and still appear homogeneous, the resultant crystals expressing the fact of solid solution by the change in their optic properties. The limit of homogeneity of the mass appeared to be reached at about 50 per cent lime and in crystals from fusions of that composition the refractive index α was found to have increased from 1·615 of pure pseudo-wollastonite to about 1·630; the optic axial angle was also larger (2 E about 20°–30°); the plane of optic axes was normal to a direction of cleavage in contrast to its position in crystals of solid solutions of the metasilicate and silica in which the plane of optic axes was observed parallel to the direction of cleavage. In the 50 per cent preparations, twinning lamellae with small extinction angles can often be seen on sections normal to the acute positive bisectrix, thus demonstrating their monoclinic or triclinic nature, notwithstanding the hexagonal outline of the basal section and systems of cleavage lines intersecting at angles of about 120°.

In products containing a little more than 50 per cent of calcium oxide the fine-grained eutectic begins to appear in small patches between the crystallites of the metasilicate. Fusions from mixtures of about 55 per cent lime and 45 per cent silica are usually fine-grained, and differences in size between crystals of the meta- and orthosilicate are less apparent.

Preparations with more than 55 per cent lime ordinarily disintegrate to fine powder on cooling, due to the great increase in volume of the orthosilicate on inverting to the γ-form at low temperatures. Studies in texture could not therefore be made in the loose powder, and evidences of solid solution near the orthosilicate were sought for by means of optical constants alone. The refractive indices of the minute crystallites from the products approaching the orthosilicate in composition were not observed to differ appreciably from those of the orthosilicate.

The products whose composition extended from the orthosilicate to pure lime were not homogeneous and contained both end members in variable amounts. If quenched quickly, the melts consisted of fine grains of the high refracting calcium oxide and the α-form of the orthosilicate; if allowed to cool slowly, the α-form inverted ordinarily to the γ-form with attendant shattering or "dusting" of the product.

Thermal evidence showed that the eutectic for the orthosilicate and calcium oxide is very close in composition to that of the orthosilicate. Preparations of this composition were examined under the microscope but no definite eutectic structure was observed. In such cases thermal evidence alone must be relied upon to determine the eutectic point, as the optical data are entirely inadequate.

Summary.—There are only two definite compounds of lime and silica capable of existing in contact with the melt. They are:

(1). The pseudo-hexagonal metasilicate melting at 1512° and inverting into wollastonite at about 1200°. The metasilicate is able to take up a small amount of either lime or silica in solid solution.

(2). The orthosilicate of calcium, which melts at 2080° and possesses three polymorphic forms:

The α-form, which crystallizes in the monoclinic system, has a density of 3·27 and a hardness of between 5 and 6.

The β-modification crystallizes in the orthorhombic system and has a density of 3·28.

The γ-modification has a density of 2·97, and also crystallizes in the monoclinic system. The disintegration or "dusting" of the orthosilicate and of all lime-silica mixtures above 51 per cent lime is due to the 10 per cent volume-change accompanying the $\beta \rightleftarrows \gamma$ inversion.

The inversion point α to β occurs at 1410°, β to γ at 675°.

There are three eutectics in the series:—tridymite+the metasilicate at 37 per cent CaO, 1417°; the metasilicate+orthosilicate at 54 per cent of lime, 1430°; and orthosilicate+lime at 67½ per cent of lime, 2015°.

The orthosilicate is readily attacked by water, which dissolves out the lime in large quantities. This is probably the reason why it is not found as a natural mineral.

The density of fused CaO is 3·32; its hardness 3+. It fuses in the electric arc but its fusion temperature is not accurately measurable. Lime crystallizes in the isometric system and possesses no polymorphic forms.

Silica begins to melt at about 1600° to an extremely viscous liquid, so that an exact melting point cannot be determined. It has been shown that for all temperatures above 1000° pure

quartz changes into tridymite, and pure quartz glass crystallizes as tridymite; so that above this temperature tridymite is unquestionably the stable phase. In the presence of fused chlorides silica crystallizes as quartz at temperatures up to 760° and as tridymite above 800°; crystalline quartz inverts to tridymite above 800° and tridymite goes back to quartz at 750°. The inversion temperature is therefore about 800° and the change is enantiotropic. The density of artificial tridymite was found to be 2·318, and that of quartz glass 2·213. The pure natural quartz used had a density of 2·654, the artificial crystals, 2·650.

Neither the salt of the trisilicic acid, $Ca_2Si_3O_8$, the åkermanite analogue, $4CaO,3SiO_2$, nor the tricalcic silicate, $3CaOSiO_2$, can exist in the two-component system.

The optical evidence gained by the microscopic study of the crystallized products of mixtures of silicon dioxide and calcium oxide in variable proportions confirms the pyrometric measurements in the following particulars: (1) That silica, calcium metasilicate, calcium orthosilicate and calcium oxide are the only compounds in the series; (2) that two different modifications of silica exist and correspond in their properties to the minerals quartz and tridymite; that the metasilicate crystallizes in two enantiotropic varieties, one of which is identical with the mineral wollastonite in its characteristics; that three enantiotropic phases of the orthosilicate exist and are stable at different temperatures; (3) that the metasilicate forms solid solutions both with silicon dioxide and with orthosilicate over limited ranges.

The experience gained in the course of the examination of these and other laboratory preparations indicates that the best results can be obtained by observing them in powdered form and immersed in liquids of different refractive indices and not in thin sections embedded in Canada balsam. In a liquid whose refractive index is equal to that of one of the component substances of the product, the differences in homogeneity in the product are more readily discerned than in a thin section, and at the same time one of the optical constants of the substance is ascertained.

Geophysical Laboratory,
Carnegie Institution of Washington, June, 1906.

Art. XXVII.—*Analysis of "Iron Shale" from Coon Mountain, Arizona;* by Oliver C. Farrington.

In the account recently published by Messrs. Barringer and Tilghman* of their investigations at Coon Mountain, Arizona, they call attention to a magnetic oxide of iron, locally known as "iron shale," which they state occurs in considerable quantity upon the mountain. The distribution of the shale is stated to be around the rim of the "crater," especially on and in its northern portion and near by on the plain. In the form of minute particles, either as fragments or as spherules, it is also said to occur over the surface of the surrounding country concentrically around the crater for perhaps several miles. Beneath the surface large fragments are found, at varying depths, the greatest depth noted being twenty-seven feet. The pieces reported by these authors varied from one to thirty pounds in weight. No quantitative analysis of the shale is given, but qualitatively it is said that all the specimens examined contained nickel to the same extent, proportionally speaking, as in the Canyon Diablo meteoric iron. It is also stated that within the larger pieces may be seen green hydroxide of nickel, while in the very minute pieces of shale the nickel has leached out to a greater or lesser extent. Occurring with the shale and believed by these authors to be related to it, are so-called "shale balls," which are described as roughly globular to oval in shape, the outside having been converted into hydrated oxide of iron, while the interior is usually magnetic oxide of iron. These are said, when broken open, to show in nearly every instance the green hydroxide of nickel. In some cases these shale balls are said to contain a solid iron center. As the magnetic oxide which surrounds this center usually presents a more or less laminated appearance, it is assumed that the so-called iron shale found on the surface, as seen on a slightly curved piece, has resulted from the alteration of the shale balls. It is also stated that the pieces of laminated oxide are often grouped, as if a shale ball or piece of meteoric iron which was once covered by a magnetic oxide of iron had fallen on the spot and the magnetic oxide of iron had been disintegrated by the fall, or afterward by atmospheric agencies. These authors apparently consider their mention of this material the first which has been published, but in Foote's account of the Canyon Diablo meteorites† mention is made of material which is probably of the

* Proc. Phila. Acad. Nat. Sci., vol. lvii, pp. 861–914, 1905; this Journal, June, 1906, p. 402.

† This Journal (3), vol. xlii, pp. 413–417.

same nature. Foote states that accompanying the pieces found at the base of the crater were oxidized and sulphureted fragments which were shown by a preliminary examination to be undoubtedly of meteoric origin. Foote secured about 200 pounds of this material, varying from minute particles up to pieces weighing 3 pounds 14 ounces. These fragments are described as mostly quite angular in character, and a few as showing a greenish constituent "resulting probably from oxidation of the nickel." The oxidized material Foote states to be identical in appearance to an incrustation which covers some of the iron masses and partially fills some of the pits. In Koenig's chemical examination published in the same paper he states that "the iron is associated with a black hydroxide containing Fe, Ni, Co and P in the ratio of the metallic part and therefore presumably derived by a process of oxidation and hydration of the latter." Foote evidently regarded the oxidation of this material as having taken place during the fall of the meteorite, as he states that "the remarkable quantity of oxidized black fragmental material that was found at those points where the greatest number of small fragments of meteoric iron were found, would seem to indicate that an extraordinarily large mass of probably 500 or 600 pounds had become oxidized while passing through the air and so weakened in its internal structure that it burst into pieces not long before reaching the earth." Barringer's view of the magnetic oxide seems to accord with this.*

In Derby's account of the constituents of the Canyon Diablo meteorite† reference is also made to what is undoubtedly this same material. Derby's statement is as follows:

"I was also shown in Washington schistose masses of iron oxide found in the same region, whose connection with the meteorite was considered doubtful. These closely resemble the thicker masses of rust crust formed on the Bendego meteorite and like it, as is well seen in sections prepared by Mr. Diller, show minute particles with a metallic luster which were almost certainly grains of schreibersite, as that mineral has been separated from the rust crust of both Bendego and São Francisco do Sul. In view of its occurrence it can hardly be doubted that these Canyon Diablo specimens are due to secondary alteration of the meteorite. As the iron masses in general have a thin rust crust, indicating considerable resistance to oxidation, it may be suggested that these thicker masses of oxide may perhaps come from original pyrite as in the case of São Francisco do Sul."

It is thus seen that this material has been observed by previous investigators, but no detailed examination of it seems as

*Op. cit. p. 882.

† This Journal (3), vol. xlix, pp. 102–110.

yet to have been published. As it seems desirable to throw as much light as possible on the remarkable character of the formation of Coon Mountain, the writer deemed it advisable to determine what information might be gained from a quantitative analysis. Specimens of what seemed to be the same material as that described by Messrs. Barringer and Tilghman were already in the Field Museum collections, but in order to be certain to obtain the material described by them, a request was made of Mr. Barringer for specimens. These Mr. Barringer very kindly furnished, in the shape of several pieces of "shale" weighing in all about half a pound, as well as one of the small "shale balls." The pieces of shale received were of flattened or elongated form, angular, and weighing a few ounces each. All showed a quite uniform blackish-brown color. On fresh fracture the color appears more nearly black, and the surface has a glossy appearance. A laminated structure characterized all the pieces. The laminae of which the shale is made up are more or less intercalated but average about one millimeter in thickness. The divisions between them are made in part by thin layers of a brownish-white substance which effervesces with acid and is undoubtedly the aragonite coating frequently observed on the Canyon Diablo siderites and described by Foote. These layers do not affect the appearance of the shale to the naked eye, however, for without a lens only a uniform color and structure is apparent. The shale is sufficiently coherent also to take a fair polish. The "shale ball" received from Mr. Barringer is in color and texture similar to the shale. Its lamination is however concentric rather than horizontal. Its form is ellipsoidal and diameter about one inch. Its surface is broken by broad, irregular cracks extending nearly to the center. Both the shale ball and a piece of the shale showed the same specific gravity, viz: 3·73. The large pieces of shale show sufficient magnetism to affect a compass needle, and small pieces are readily attracted by a common horseshoe magnet. The shale crushes rather easily in a mortar to a dark brown powder. This powder is also quite magnetic. Heating in a closed tube causes considerable water to be given off, showing that a hydrous oxide is present. The material appeared, therefore, to be referable neither to magnetite nor to limonite, since it was too magnetic for limonite and contained too much water for magnetite. None of the specimens showed the green hydroxide of nickel referred to by Foote and Barringer. Only the powder which was attracted by the magnet was used for analysis, but this included practically all of it. The analysis by Mr. H. W. Nichols gave the following results:

Fe_2O_3	74·63	Al_2O_3	0·05
FeO	3·91	SO_3	0·00
NiO	9·79	S	tr.
CoO	0·49	P_2O_5	0·00
CuO	0·00	P	0·10
CaO	1·27	C	0·15
MgO	0·00	Cl	0·08
			99·93
H_2O	8·02	O=Cl=	0·01
SiO_2	1·09	O=P=	0·15
CO_2	0·35		99·77

The results of this analysis confirm the statements of Koenig and Barringer that nickel and cobalt are to be found in the shale in the same proportion as in the meteoric iron, and leave little doubt that the "shale" is derived by oxidation from the meteoric iron. It is obvious that the analysis may be interpreted in several ways, since much uncertainty exists as to what changes iron undergoes in the process of "rusting." By some it is thought that a ferrous carbonate is first formed which later alters to ferric hydroxide. Others doubt the influence of carbonic acid and believe that the oxygen and water of the air produce ferrous oxide and hydrogen peroxide. By the first process it would be expected that limonite alone would be produced, while the second might form some magnetite. Examination under the microscope of the finely powdered shale showed differences of color and texture not observable to the naked eye. In the small grains appeared alternations of black and yellow colorings and compact and earthy textures which suggested associated magnetite and limonite. The analysis calculated on this basis gives fairly satisfactory results. By assuming that all the protoxide of iron and nickel is present as a constituent of magnetite, and that the remaining sesquioxide and water are present as limonite, the different constituents can be fully accounted for. Such a constitution also explains the magnetic character and color of the powder. Calculated in this manner and grouping the minor constituents according to their apparent origin, the following constitution of the shale is indicated:

Limonite	52·99
Magnetite	42·39
Schreibersite	0·64
Graphite	0·15
Lawrencite	0·14
Aragonite	0·80
Andradite	2·45
Quartz	0·21
	99·77

The andradite here reported was not observed, but its presence was indicated by the percentages of lime, iron and silica remaining after the deduction of the other constituents. That it could readily become mixed with the shale from the surrounding sands seems probable. The other constituents indicated are readily referable to the accessory constituents of the meteorite and the results of the analysis are of interest as showing what changes take place in them. The Canyon Diablo meteorites, as is well known, contain as accessory constituents, troilite, graphite, cohenite and schreibersite. Of sulphur, representing troilite, only a trace was found. It appears, therefore, that sulphates were formed and leached out. No phosphorus was found to be present as phosphates and only 0·64 per cent as phosphides. It thus appears that while some schreibersite remained, all which had oxidized to phosphate had been removed. The percentage of carbon found, 0·15 per cent, indicated some cohenite or graphite yet remaining. The percentage of chlorine found indicates the presence of lawrencite, to which, as shown later, may be ascribed probably to some extent the oxidation of the meteorite. The percentage of nickel oxide found is somewhat higher than usually reported for the Canyon Diablo meteorites and suggests that a concentration of nickel oxide has taken place through a greater solubility of the iron. It is well known that taenite, which is the more highly nickeliferous constituent of nickel-iron, resists oxidation longer than kamacite, and this might tend to increase the nickel content of the oxidized product. Whether the nickel oxide when formed would be removed more or less rapidly than the iron oxide does not seem to be known as yet however. Test was made for metallic iron and nickel in the shale by treating the powder with iodine, but practically no indications of the presence of these constituents were thus obtained. The shale also when immersed in a solution of copper sulphate showed no deposition of copper such as would occur if the above metals were present. Undoubtedly pieces of the shale in which oxidation had been less complete would show such a content.

Comparison of the analysis of the shale with those of rust crusts of other meteorites made by other authors shows differences chiefly in the percentage of water found. Thus Pugh, in the crust of Toluca,* Haushofer in that of Cranbourne† and Cohen in that of Beaconsfield‡ found an amount of water approximating closely to 13 per cent. This indicates

* Inaug. Diss. Göttingen 1856, pp. 5–14.
† Jour. pr. Chem. cvii, pp. 330–331, 1869.
‡ Meteoritenkunde, Heft ii, p. 263.

an alteration of the iron to limonite. It is not stated whether these crusts were magnetic or not. The amount of NiO and CoO found by Cohen in the Beaconsfield crust was only 1·68 per cent, and by Haushofer in Cranbourne 3·1 per cent. In these cases a leaching of the nickel-cobalt oxides has apparently occurred. It is probable that different climatic conditions would have considerable influence in affecting the composition of such rust crusts.

Explanation of the origin of the laminated structure of the shale is doubtless furnished, as suggested by Barringer, by the shale balls. Oxidation and hydration proceed from the surface inward. These changes cause an increase in bulk of the layers successively reached in the process, so that they separate slightly from the unchanged material beneath, and interstices are afforded through which the oxgyen and water enter to attack the metal. Thus the process is continuous and depends only on time and exposure for its completion. The cracks in the shale balls show that the present superficial layers once covered an interior which has since increased in bulk.

If it be accepted that the iron shale and shale balls are oxidation products of an ordinary Canyon Diablo siderite, it remains to be determined why certain of these siderites should have so oxidized while others have not. One reason is probably to be found in the observation of Barringer that the iron shale often occurs beneath the surface, while the meteoric irons are found only at the surface. Those meteorites which were covered more or less by soil and rock fragments would receive a larger supply of water and hence would suffer more rapid oxidation and hydration than those at the surface. It may also be true that the individuals which have decomposed to form shale balls and shale contained more lawrencite than those which have not. Barringer states* that "the iron centers of the shale balls nearly always show a peculiar oxidation of drops of moisture, often colored green, partly perhaps from the presence of nickel. This exudation, Dr. Mallett explains to me, is due to the presence of chloride of iron." It is well known that among the Toluca meteorites, for example, some individuals contain a considerable amount of lawrencite while others do not. The former "sweat" and rapidly decompose, even in a museum case, while the latter remain dry and unaltered. Mr. Nichols has called my attention to a continuous decomposing action probably exerted by lawrencite which has perhaps not been noted before in this connection. Ferrous chloride in contact with air and water forms ferric hydroxide and chloride:

$$6FeCl_2 + 3O + 3H_2O = Fe_2O_6H_6 + 4FeCl.$$

*Op. cit. p. 882.

The ferric chloride is, however, reduced by contact with iron to form ferrous chloride again:

$$4FeCl_3 + 2Fe = 6FeCl_2$$

so that the process is continuous. In addition there may occur a formation of free acid through hydrolysis of ferric chloride:

$$4FeCl_3 + 6H_2O = Fe_2O_6H_6 + 6HCl + 2FeCl_3.$$

This acid would obviously likewise exert a decomposing action.

In conclusion, it may be said that the view of Foote and Barringer that the oxidation which produced the "shale" took place during the fall of the meteorite, is not that of the present writer. In the present writer's view the oxidation occurred subsequent to the fall of the meteorite, and was so gradual that the production of the shale can be explained only by assuming that the fall took place many years ago.

Field Museum, Chicago, June 15, 1906.

Art. XXVIII.—*Of the Phenomena Observed in Crookes' Tubes;* by N. T. Bacon.

No satisfactory explanation seems to have been made of the phenomena characterizing prolonged discharges in a Crookes tube.

Results which have been recognized are A, discharge of peculiar rays from the anode; B, discharge of different peculiar rays from the cathode; C, gradual attenuation of the discharges; D, recrudescence of the discharges on heating the walls of the tube; and E, coating of the walls with platinum black.

The attempt has been made to explain C and D by supposing the vacuum to increase, beyond the point where the discharges can pass, by absorption in the pores of the glass walls of portions of the residual gases, and rediscbarge of these on heating the tube. But this hardly seems rational. It is contrary to all our ideas that an intense vacuum should be intensified by absorption of gases in the walls of the containing vessel in which the vacuum was originally produced. We should expect instead a slow evolution of relics of the greater amount of the same gases absorbed in the body of the glass under the higher original pressure; and furthermore, if any such effect existed, it could hardly fail to result in a kind of osmotic transfusion from the outside, where, as in this case, the containing wall is often not over $\frac{1}{10}$ inch thick. It seems reasonable to ascribe the gradual attenuation to increasing vacuum, as it is partly overcome by heating the walls of the tube. Glass is known to have (and particularly with aqueous vapor) the property of accumulating over its surface a film denser than the average of the surrounding atmosphere, and this is even more marked with platinum. This I lay to lack, in the solid state, of the perfect elasticity of the molecule, which is postulated by the received theories of gaseous tension. Why should we not consider molecular elasticity to be more or less imperfect in the solid state? We should then find a ready explanation of the heating of platinum sponge in an atmosphere of hydrogen, accompanied by condensation of the hydrogen even to the point of liquefaction. The molecule of hydrogen striking the imperfectly elastic platinum molecule would rebound with diminished velocity, the lost kinetic energy going to raise the temperature. In the pores of platinum sponge the hydrogen molecule will naturally strike again and again the imperfectly elastic mass, with further evolution of heat and loss of velocity, until it reaches nearly the orbital velocity of the vastly heavier platinum molecule, thus being reduced even to

the liquid condition. Subsequent molecules of hydrogen would suffer like losses (though less rapidly, owing to occasional impacts on hydrogen instead of platinum) until a film of hydrogen molecules should form a more perfectly elastic coating, and equilibrium would be established (with higher temperature in the film than in the surrounding atmosphere) when impact on the platinum of a fresh molecule of hydrogen raised the temperature of the film to the point of expelling another molecule from its surface. Evidently such a film would give off molecules when heated, and knowing platinum black to have this action on gases in higher degree than glass, we can see how the vacuum might be increased by the platinum coating, and why heating the walls of the tube should have the effect of partially restoring its activity. It is also interesting to note that by this theory the higher the vacuum the more important relatively this action becomes, as the exposed surface of imperfect elasticity remains constant, while the number of gaseous molecules diminishes, and thus the ratio increases of impacts resulting in loss of velocity.

This may sufficiently explain the recrudescence on heating the walls of the tube, but does not explain the emission of rays, and hardly seems sufficient for the continuing gradual increase of vacuum. Why should not these be accounted for on the hypothesis of a resolution of atoms into electrons or emanations under the discharge in a Crookes tube, and radiation of these (to which the glass walls might be pervious, more or less, as to the ether, though entirely impervious to molecular matter) of different polarity from the different electrodes? Of these rays we know very little, except that they differ materially from the forces with which we are accustomed to deal. The X-rays, emanating from the anode, are absorbed by mass apparently much in the way that light is absorbed by partially transparent substances, as is shown by the X-ray pictures, and they have been considered (though perhaps on insufficient grounds) to have also the velocity of light, which would tend to suggest their relation to the electric current streaming also from the anode; but no ordinary reflection or refraction of them is possible. On the other hand, about all that we know of the cathode rays is that they can be deviated by a magnetic field, thus showing some of the characteristics of mass, and, moreover, they seem to move more slowly than light.

We are not reduced here to consideration of the electron solely. Possibly we may have to do with one or both of the still more ethereal forms of matter postulated to account for the curious changes attending the transformation of radium to helium, but, from present indications, is it not probable

that, under these limiting conditions, the electric discharge can only take place by a disruption of atoms (failing chemical combinations, of which after electrolysis of the residual aqueous vapor probably none would remain) similar to the electrolysis, which alone enables the current to pass through water and other liquids?

There is, of course, the intermediate possibility of the mere disruption of molecules into nascent atoms, but this probably would not continuously intensify the vacuum by enabling the elements to escape, though it might be an intermediate stage.

The extremely tenuous condition of the residual elementary gas or gases in a Crookes tube, reducing exchanges of charges to a minimum, would apparently be a favorable condition for such disruption, and probably the high temperature would be another.

Holderness, N. H., Aug. 18, 1906.

Art XXIX.—*Northward Extension of the Atlantic Preglacial Deposits;** by Isaiah Bowman.

Outline.

Introduction.
Lithologic and Structural Features.
  Preglacial Series.
    (1) Basal Clays.
    (2) White and Yellow Sands.
    (3) Red Sands.
    (4) Dark Green Sands and Clays.
  Glacial Series.
    (1) Stratified Deposits.
    (2) Unstratified Deposits.
Succession of Events in the Deposition of the Third Cliff Beds.
Former Interpretations.
Occurrence of Preglacial Deposits near Third Cliff.
Correlation with similar Deposits farther South.
  Continuity of Deposits.
  Similarity of Materials.
  Paleontologic Evidence.
Conclusion.

Introduction.

Heavy winter storms on the New England coast following the unusually dry autumn of 1904 resulted in many changes in coastal topography, among which were the rapid cutting back of headlands of soft material and the freshening of cliffs. Good opportunities were thus presented for the study of exposed geological sections. The Third Cliff section near Scituate, Massachusetts, is of special interest because of the lithologic and stratigraphic homologies between the exposed beds and preglacial deposits farther south and their bearing on the question of the northern limit of the Atlantic Cretaceous and Tertiary. The nearest known outcrop of deposits of Cretaceous age is at Gay Head, Martha's Vineyard, 52 miles south of Third Cliff; the nearest known deposits of Tertiary are the Miocene Greensands at Marshfield, 7 miles south of Third Cliff. The latter are not commonly known to occur though they were noted by Hitchcock† as early as 1841 (p. 91), the latest text-book of Geology‡ stating that "The northernmost exposure of the Miocene on the Atlantic coast is on Martha's Vineyard."

Third Cliff is one of a series of four cliffs in close succession twenty miles southeast of Boston and immediately south

* The suggestions of Professors Woodworth and Jaggar of Harvard and Professor Barrell of Yale University are hereby gratefully acknowledged. Special thanks are due Professor Jeffrey of the Harvard Botanical Laboratory for identifying the lignites.

† Final Report on the Geology of Massachusetts, vol. i, pp. xii to 831, 1841.

‡ Geology, Chamberlain and Salisbury, vol. iii, p. 260, 1906.

of Scituate Harbor. They are represented on the Duxbury Sheet, U. S. G. S., as the eroded edges of drumlin-shaped hills, from 20 to 75 feet high and with major axes trending NNW. The accompanying sketch (fig. 1) of a part of Third Cliff depicts the chief features referred to in the following description.

Lithologic and Structural Features.

Preglacial Series. (1) *Basal clays.*—The basal member of the Third Cliff section is a layer of clay having the light yellow color of terra cotta. The top of the layer is about at the level of high tide, and an excavation of several feet failed to reach the bottom. It lies in a nearly horizontal position, with slight dip to eastward. It is extremely unctuous when wet and resists wave action to such a degree that

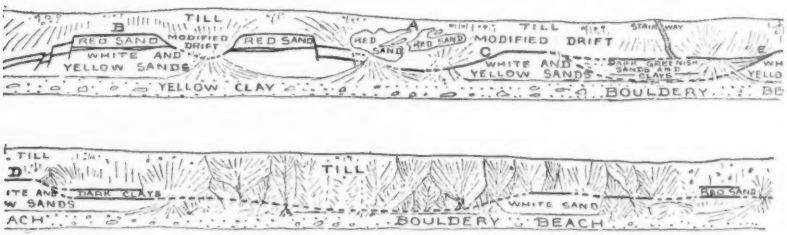


FIG. 1. Topography and structural relations of part of Third Cliff. Heavy continuous lines represent observed structures. Heavy dotted lines represent inferred structures. Horizontal scale = 175 feet to the inch. Vertical scale = 130 feet to the inch.

the height of the steeply-sloping bowlder-strewn beach (fig. 1) is determined by its upper surface. Within the body of the deposit the clay is very pure, but towards the top becomes more sandy, containing round inclusions of yellow sands up to a centimeter in diameter. Lamination appears near the upper surface, at first faintly and then more strongly marked, changing finally into cross-bedded structure, although the bulk of the material is still clay. An 18-inch deposit of alternating yellow sands and clays, of several inches thickness each, completes this lowest member of the preglacial series. The entire layer contains muscovite in considerable quantity, and under the microscope shows an occasional grain of glauconite and scattered fragments of sponge spicules, none of which have sufficient character to be identifiable, although one specimen suggested a form of *Geodia*.

(2) *Yellow and white sands.*—A deposit of yellow and white sands lies conformably upon the basal clay, the latter color gaining predominance towards the top. Like the clays

beneath them, these sands dip gently to the eastward. Their maximum thickness is 25 feet, with, however, many variations in thickness, as will be explained in a later paragraph. But slightly cross-bedded at the base, these sands become more and more irregular towards the top, where they display excellent cross-bedded structure, the upper eight feet of the layer being exclusively of this character. The sands vary in texture from fine at the bottom to coarse at the top, and show in the same direction a decreasing amount of the clayey constituent possessed throughout. Just above the clays on which they rest the sands carry sufficient clay to render them somewhat plastic when wet. At the top of the sands where cross-bedding is most marked the sands are dry and partially indurated, so that the eroded edges retreat with a nearly vertical face. The indurating process has been carried so far in a few places that the material might almost be called a sandstone. Scattered fragments of sponge spicules occur here as in the clays previously described, and an equal amount of glauconite. The sands are very silvery in general appearance, owing to the great amount of muscovite present, some of the flakes attaining a size of from 4 to 6 millimeters. There is no break in the series thus far described, every change being slow with conformable relations throughout.

(3) *Red sands.*—At the top of the white sands an unconformity occurs, the eroded edges of the white sands being overlaid by a layer of coarse and dark red sands with a maximum thickness of 10 feet. These red sands bear large quantities of muscovite, a smaller quantity of biotite, and also exhibit cross-bedding of a much greater degree of amplitude than that shown in the white sands. Occurring only in patches between the white and red sands and never present where unconformable relations between these two members are exhibited, is a thin layer (1 or 2 feet) of black, coarse sand composed of large grains of smoky quartz and with an admixture of biotite. It is cross-bedded after the manner of the red sands which overlie it.

(4) *Dark green sands and clays.*—If fig. 1 be consulted, it will be seen that below the stairway near the middle of the figure the section shows greenish black sands and clays at the level of the white sands and below the level of the red sands. The whole face was so masked by talus and landslide material near the top of the bluff that extensive excavation was necessary to determine the relations of the various beds. Both series of beds were evidently in place and the problem resolved itself into finding the line of contact between the two. This was accomplished with the results shown in fig. 2, which is an enlarged portion of fig. 1 at E.

The white sands were found to exhibit in the clearest possible manner the erosion of a considerable body of their material, the entire series above them being swept away in addition. Upon their eroded edges lies unconformably a layer of white and yellow clays and sands which are superseded above by the greenish black clays noted in the section. The overlying dark clays and the yellow sands and clays between them and the underlying white sands, thicken gradually toward the middle of their outcrop (fig. 1), where the sands attain a maximum thickness of 3 feet and the clays 8 feet. These clays exhibit

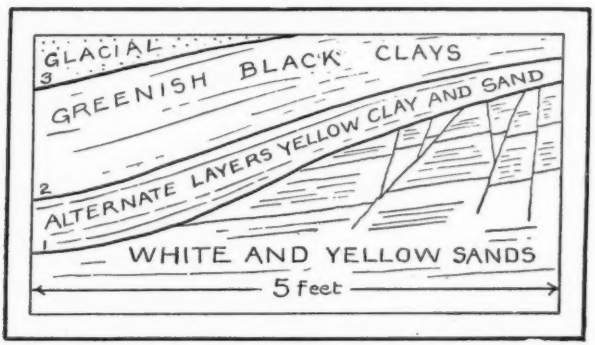


FIG. 2. Representing unconformity between dark clays and white and yellow sands at E, fig. 1. Nos. 1 and 3 in diagram represent unconformities; at 2 the deposits are conformable.

the same changes as those of the lowest clays in the series—a gradual transition into more sandy members of similar color and 12 feet thickness, which completes the upper part of the preglacial section.

As soon as this relation between the beds was discovered the entire section was re-examined with a view to interpreting the relations which proved puzzling elsewhere, and in each locality, no matter how disturbed by ice action or disguised by landslides, the greenish-black clays and sands were always found upon excavation to overlie stratigraphically the white sands of cross-bedded structure.

Glacial Series.—The glacial material which overlies all of the preceding beds may be divided into two classes. The lowest is stratified brown sand bearing a high percentage of erratic material and occupying the eroded depressions in the lower beds; the second is a confused mass of red and white sands (see A, fig. 1) intermingled with erratic sands and typical bowlder clay, the bowlders attaining a maximum diam-

eter of 6 feet. The two classes of deposits are in unconformable relation to each other, and along the entire cliff face are seen to be in strong unconformity with the beds on which they rest (see B, C, D, fig. 1). The detailed structure of the till is shown in fig. 3, great blocks of bowlder clay being separated by a "filling" of horizontally stratified sand which, being without the slightest marks of disturbance since deposition, was deposited in water either contemporaneously with the till or later as a secondary deposit between the blocks of till as fast as the ice between the blocks was melted out. At Fourth Cliff similar structures are seen with a considerable part of the material derived from the preglacial beds eroded by the ice sheet in its advance. At Indian Hill, seven miles southeast of Plymouth, a good 85-foot section shows the further complexity of a layer of clay entirely different than any in the Third Cliff section, with a thickness of 20 feet and underlaid by erratic sand and gravel.

FIG. 3. Showing structure of till just beyond left margin, fig. 1. Sand between till blocks is cross-bedded and undisturbed. Figure represents area about 5 feet square.

This layer may represent an interglacial deposit or a deposit formed during a temporary recession of the ice. Its homologue does not exist in the Third Cliff section, nor is there any indication whatever at the present time of deposits or structures developed contemporaneous with those at Indian Hill. In all three sections there exists a thin layer of iron-stained reddish and apparently older till just above the stratified material of aqueo-glacial origin.

Succession of Events in the Deposition of the Third Cliff Beds.

The points to be considered in the determination of the age of the beds below those of glacial relationships will be better understood after their interpretation in terms of the events which they represent.

It appears that we have represented in the 40 or more feet of yellow clays and sands first described, marine conditions with a steady shallowing of the basin of deposition either through uplift or the gradual upbuilding of the floor through sedimentation. These conditions are marked particularly by the sand inclusions which occur on the top of the clays and the gradual transition of clay to sand with the upper part of

the sands strongly cross-bedded. There followed a period of erosion which may represent very shallow water conditions without actual exposure to subaërial processes. Currents and waves have already found expression in the cross-bedded structure and to their increased efficiency at this time may be attributed the unconformity in question. Then came the deposition of the black sands composed of grains of smoky quartz, followed by the deposition of the red sands. The slight thickness of the beds representing the intervals of deposition, together with their cross-bedded structure and present position and attitude with respect to other beds, and the existing shoreline favors the view that coastal changes were here of a less profound order than along the more southerly part of the Atlantic littoral, where extensive denudation followed the deposition of beds of great thickness.

Apparently the greatest erosion followed the deposition of the red sands. In many places the red, black, and white and yellow sands are entirely removed down to the basal yellow clays. In the depressions thus formed was deposited the greenish black clay of figures 1 and 2. Gradual shallowing of the deeper water in which the clays were deposited is represented by the greenish-black glauconitic sands at the top of the darker beds, figure 1.

The succeeding events of importance in the history of this part of the New England shoreline were the erosion of the whole series thus related and successive advances of the ice. The first effect of the latter process was probably the deposition of the brown erratic sands as a preliminary wash to be superseded by the deposition of the ice-borne clay and bowlders. The relations of the glacial material were not considered in detail, as the field of observation was too limited. The explanation of the manner of deposition of the stratified glacial sands may therefore be erroneous when more extensive observations are made. The retreat of the ice left the surface of the till practically as we see it today, except where it is modified by shallow gullying or by the insistent attack of the sea.

The weight and movement of the ice upon the unindurated preglacial sands and clays below resulted in the bodily removal of great masses of these deposits. They are clearly seen in the face of the cliff surrounded by erratic sands and bowldery clay (A, fig. 1). In addition, the remaining sands exhibit ice disturbance, for while they are practically in situ they are minutely fractured and faulted as shown in the upper right hand corner of fig. 2. In every case the blocks are easily restored in thought to their original positions by the help of slight variations in color and texture. The openings between

blocks are filled in some cases by a silty deposit which can in every instance be traced up to the till or sand above, from which it was derived by percolating waters. The great bowlders in the till are continually falling from the cliff face to the beach below and give added protection to the basal clays which determine the level of the beach. The clays, the partially indurated sands and the till—all alike possess sufficient tensile strength to stand in bold cliffs and thus yield under an encroaching sea a remarkably clean and perpendicular section.

Former Interpretations.

Both Third and Fourth Cliffs have been described by Upham.* As his interpretation differs widely from the one just given, the following summary of his results seems appropriate in this place. It should be said that the section is today in much better condition than when examined by Upham and probably shows the relationships of the various deposits very much more clearly than at any time heretofore.

The two cliffed hills are referred to as "two extraordinary drumlins . . . . which consist of till . . . . to a depth that varies from 15 to 25 feet . . . . but below include beds of modified drift that attain in Third Cliff a thickness of at least 40 feet, reaching to the bowlder-strewn shore . . . . ." Neither the yellow clays which, partly masked by bowlders, form the shore, nor the unconformities above and in the so-called modified drift were noted. That the material is not modified drift is shown by a wholly dissimilar structure and lithologic character; and by the total absence of erratic material, and a remarkably pronounced and persistent unconformity between the erratic and non-erratic beds, with several smaller unconformities within the latter (see conclusion, p. 325).

Upham speaks further of the anticlinal structure of the modified drift and the approximate coincidence of the upper surface of these beds with the surface of the till at the cliff top. This is offered as evidence of the manner in which drumlins are deposited underneath the ice, but in the better section of today the cliffs show in the clearest possible manner that the apparent anticlinal structure is in reality the effect produced by successive faultings of broken blocks of white and red sands as shown near the left margin of fig. 1; and that the coincidence or parallelism of the structural surfaces called anticlinal is due not to similar dynamic conditions imposed by the ice, but to the control exercised on ice movement and deposition by the form of the subjacent terrane. It cannot, therefore, be argued alone from the relations exhibited here that drumlins are a subglacial deposit built up by successive accretions from the debris-laden lower part of the ice. It is

* "The Structure of Drumlins." B. S. N. H. Proc., xxiv, 238-242, 1889.

not implied that such conditions may not have occurred elsewhere, but that such was not the case here is clearly proved.

The presence of the yellow sands was noted by Upham and also the lignitic clays, "laminated dark gray clay," the latter being attributed to deposition of material subglacially transported, the lignites being explained as the possible remnants of an interglacial forest overwhelmed by the ice, yet the absence of all bowlders and till fragments in the clays was observed. The better section of today shows also that the structure of the till is in reality like that shown in fig. 3, and not obscurely laminated. The same figure shows the presence of seams and lenses of gravel within the till, their absence having been asserted heretofore. The various anomalies, which Upham's observations led him to believe were present here, were explained by the suggestion that the modified drift of Third Cliff was deposited under very unusual sub-glacial conditions.

Occurrence of Preglacial Deposits near Third Cliff.

Deposits of pre-Pleistocene age once subaërially eroded and now submerged have been presumed by several writers to occur near shore on the floor of the sea north of Martha's Vineyard. The first to suggest this, with the possible exception of Hitchcock, who vaguely refers to this matter (p. 427), was Verrill,* who observed in dredged material from the north Atlantic coast compact calcareous sandstone and arenaceous limestone bearing fossil shells and fragments of lignite. About half the fossil forms were considered extinct. Verrill thinks that the fragments were probably "detached from a very extensive submerged Tertiary formation at least several hundred miles in length, extending along the outer banks, from off Newfoundland nearly to Cape Cod and perhaps constituting, in large part, the solid foundations of these remarkable submarine elevations."

Later on, Upham† reports finding fossils of possible Eocene or Cretaceous age in the drift materials near Highland Light, Cape Cod. Hitchcock‡ even believed from the Miocene deposits at Marshfield (seven miles south of Third Cliff) that deposits of Tertiary age occurred "abundantly along the coast from Marshfield to Plymouth and not improbably also on Cape Cod," although their actual occurrence was not noted.

Professor Shaler, in his report on the geology of the Cape Cod District,§ suggested the presence, at least on the sea floor,

* "Occurrence of Fossiliferous Tertiary Rocks on the Grand Bank and George's Bank." This Journal (3), xvi, pp. 323–324, 1878.

† Marine shells and fragments of shells in the till near Boston, B. S. N. H. Proc., xxiv, pp. 127–141, 1889.

‡ See footnote, p. 9.

§ "The Geology of the Cape Cod District," by N. S. Shaler, 18th Annual Report, U. S. G. S. Part II, p. 580, 1896–97 (see also pp. 516 and 578).

of Cretaceous and Tertiary deposits northward as far as Cape Ann, from the general likeness of the outlines of the shoals of Stellwagen Bank to Cape Cod and the relations of the now submerged valleys.* The suggestion, though a purely analogous one, is of great interest in the further exploration of the field concerned.

Correlation with Similar Deposits to the South.

The evidence upon which age determinations are attempted is gathered from a close study of the strata themselves and of adjacent areas. The paleontologic evidence secured does not have the specific quality demanded for the purposes of correlations, although none of the evidence of this nature negatives the conclusions reached by other evidence. In short, the conclusions rest upon presumptive evidence and must, therefore, be held as tentative and suggestive only.

Continuity of Deposits.—At Marshfield, seven miles south of Third Cliff, greensand beds were noted by Hitchcock as early as 1830.† Their age was later determined by Dr. Dall from fossil evidence and found to be Miocene. The deposit is highly glauconitic, occurs about up to 15 feet above mean tide level, and is in very close contact with the granitic floor, which outcrops two miles farther south. The sands do not outcrop, but are reached by excavating 6 to 8 feet beneath the surface. They were first discovered in digging for a well on the farm of Mr. Kent.

The presence of this bed suggested that coastal sections between Third Cliff and Martha's Vineyard might show similar deposits, but a search from Boston Harbor to Peaked Cliff, 15 miles southwest of Plymouth, proved fruitless except for the finding of drift material often in great abundance derived from preglacial beds undoubtedly similar to those at Third Cliff. This is particularly true of parts of the glacial deposits at East Marshfield, Kingston, Indian Hill, Lookout Point, and Peaked Hill. The unusual character of some of the glacial material in these places is very striking. There is a large amount of white and red sand rather poorly mixed with the more common brown sand noted in sections of glacial material farther inland. These suggest the wider extent of the preglacial deposits and their considerable erosion by ice.

Similarity of materials.—The fact that at least a part of these deposits were formed in relatively shallow water near shore, as shown by the cross-bedded structure of the lower sands, renders their correlation on this ground along with similar deposits on Martha's Vineyard insecure, because of

*See map of the Cape Cod District.

†"Final Report on the Geology of Massachusetts," pp. 91-95, and 427, 1841.

the varying physical conditions under which sedimentation takes place in shallow waters. Controlled by the evidence of the unconformities it has, however, a more certain value. The relative thinness of the deposits close to this, their northern limit, and the frequent unconformities point to even greater irregularity in the physical conditions here than farther south, the deposits being more readily affected by slight oscillations of level common to the lands. The complexity of the mutual relations of coastal deposits is enhanced by the fact that continued erosion and redeposition often results in the close lithologic resemblance of beds of quite different age. In such cases there is, therefore, small value in the conclusions based on evidence of this sort. Unconformities and fossil evidence are the closest available determinants under such circumstances, and it is quite largely on the former that the conclusions of this paper are based.

The nearest known outcrop of beds lithologically similar to those at Third Cliff is at Gay Head, Martha's Vineyard. These are described by Professor Woodworth,* who mentions the following characters of the successive beds:

Lower Cretaceous: non-marine, lignitic, leaf-bearing clays.

Upper Cretaceous: locally hardened bands of sands containing molds of fossils, locally developed beds similar to those at Indian Hill (M. V.) which have a texture varying from fine to coarse with scattered larger grains of quartz and abundant muscovite scales. Inferred unconformity between Lower and Upper Cretaceous.

Miocene: thickness varies from 0 to 10 feet. Consists of two members—osseous conglomerate and foraminiferal or greensand beds, with unconformity between. The former is from 12 to 18 inches in thickness, consists of rounded bowlders or of nut-sized quartz pebbles white and well-rounded. Cetacean bones present. The foraminiferal bed is from 0 to 10 feet thick, green color below, brown above, basal part includes rolled fragments of osseous conglomerate and bears glauconite casts of *Macoma lyelli* in the attitude of growth and the crab *Archeoplox signifera* in lower part of stratum.

Probable Pliocene: yellowish green and brownish clays bearing glauconite and Pliocene fossils. Inferred unconformity between Pliocene and Miocene.

The paucity of glauconite in the Gay Head Upper Cretaceous and the variable texture of the material, the scattered quartz grains, abundant muscovite scales, correspond precisely with the conditions found in the white and yellow sands which form the basal member of the Third Cliff section. Even the occurrence of cross-bedding on a small scale in the coarse pre-

* "Unconformities of Martha's Vineyard and Block Island"; B. G. S. A., viii, 197–212, 1897.

Tertiary sands (p. 200) is noted. Were lithologic identity alone a determinant in correlation, we should be completely justified in calling these beds Upper Cretaceous. The irregularity of the New England shoreline, and the considerable distance (52 miles) between Third Cliff and Gay Head, make it probable that the physical conditions under which sedimentation took place were not persistent throughout the entire district, and it is, therefore, not surprising that at Third Cliff there should be present a layer of red sand cross-bedded throughout on a large pattern which does not appear in the Gay Head section. With this exception the beds overlying the first unconformity at Third Cliff are again similar to those at Gay Head, except for the osseous conglomerate which is not present at Third Cliff, but the glauconitic sands are present bearing the white well-rounded quartz pebbles. Moreover, these beds are at precisely the same altitude as those definitely known to be Miocene (p. 321) at Marshfield, seven miles south. The Marshfield beds rest upon granite, the dark sands and clays of Third Cliff upon white sands. On the whole, the relatively close agreement of unconformities and lithologic characters seems very striking. While this resemblance, as was noted on the preceding page, may have slight value on account of marginal redeposition without the destruction of characteristic features, it is in a measure significant on account of the distinctness of the separating planes in the deposits and the strongly marked individual character of each bed. It is the more convincing to one who has seen the Atlantic Cretaceous and Tertiary farther south and has noted the persistent and distinctive character of these deposits.

It would be quite unsafe to base a correlation of the Third Cliff deposits with those of New Jersey entirely on the evidence presented here, but it is not without interest to note that with a single exception the Red Bank sands occur exclusively in the Monmouth formation, Upper Cretaceous, "except in certain marginal phases of the Rancocas formation,"* which latter is itself of Upper Cretaceous age. Glauconite occurs in great abundance in the Upper Cretaceous of New Jersey, and but sparingly at Gay Head, and certain yellow sands are found alike in the Miocene and Upper Cretaceous.

Paleontologic Evidence.—A fourth probability is suggested by the studies of T. C. Brown of Columbia† on the Chappaquiddic fauna from Martha's Vineyard. A comparison of this fauna with the Eocene faunas of the Atlantic and Gulf provinces indicates that the species closely resemble those

* Upper Cretaceous Formations of New Jersey, W. B. Clark; B. G. S. A. viii, 313–358, 1896–97.

† A New Lower Tertiary Fauna from Chappaquiddick Island, Martha's Vineyard, Science, New Series, vol. xxi, No. 548, pp. 990–991, 1905.

found in the lower Eocene, and they are accordingly designated as lower Eocene. The fossils are found in ferruginous concretions, reassorted and deposited in their present position as glacial drift. They have apparently been moved from the north, probably from the sea bottom, and raise the question as to their relation to the Third Cliff deposits. Their relation is, of course, obscure at present, although future dredgings and soundings may throw some light on the subject.

As has been noted before (p. 321) fossil evidence is almost wanting. The sponge spicules, as already noted, were not identifiable with any degree of certainty. Their value even when identifiable is rarely great. The impression of a single bivalve was noted in the red sands, but as only the rounded and partly obliterated outline was visible it also proved of no value. Fortunately the green glauconitic sands in the upper part of the preglacial series are lignitic and a number of excellent specimens of pyrrotized lignite were obtained. These were carefully examined for me by Dr. E. C. Jeffrey, of the Harvard Botanical Laboratory, to whom I am greatly indebted for a statement of his conclusions, based on extensive comparative studies of lignites from Martha's Vineyard, Staten Island, and Germany. Dr. Jeffrey states:*

"The lignites from the cliffs at Scituate . . . . belong to an ancient type of Pityoxylon, earlier than that found in connection with the Baltic (Oligocene) amber. They closely resemble, although are not identical with, Pityoxylon from the Cretaceous beds of Staten Island and Martha's Vineyard, and are of the same general antique type. . . . . all of the material belongs to one species . . . ."

The fact that but one species was identified makes correlation based on the above determinations quite insecure. From the paleontologic evidence the deposits might be placed anywhere between the lower Cretaceous and the Pliocene with probabilities pointing to Eocene or Oligocene. On the other hand, the lithologic and stratigraphic evidence coupled with the geographic position of the deposits with respect to the Marshfield greensands points to their Miocene age.

In general, plant remains are known to have a low value as time markers in the geological column, especially such low forms as Pityoxylon† and allied species. The presence of the former is therefore to be considered not as confirmatory but as presumptive evidence which does no violence to the conclusions based on stratigraphic grounds.

Conclusion.

The conclusions reached after an examination of the foregoing evidence may be stated as follows:

* Personal letter, March 5, 1906.

† See Palaeophytologie, Schimper and Schenck, p. 874.

(1) The lower part of the Third Cliff section is preglacial. This is based on the character of the deposits, the entire absence of erratic material, and the relation and sequence of the unconformities. The suggestion that these beds may be interglacial is opposed by a number of facts which point to the improbability of this occurrence. In the first place, two marked unconformities such as occur within the lower deposits, together with the individual character of the different beds, indicate a distinct even if small change in the conditions of deposition which one would expect should be marked elsewhere by deposits of a similar nature. No interglacial deposits of this character are known on the Atlantic coast. It would be singular, though not impossible, that an interglacial deposit of this thickness should elsewhere be swept away, a single remnant preserved in this locality only. It is more reasonable that extensive Cretaceous and Tertiary terranes should be removed leaving here and at Marshfield and Gay Head remnants of a similar nature. It would be very peculiar indeed if an interglacial deposit were to simulate so closely the stratigraphic succession and lithologic qualities of beds of known Cretaceous and Tertiary age, and at the same time be the sole representatives of their kind on the coast. To this fact we may add that the oldest known bowlder bed in New England is present here (see p. 317) and that it occurs above the unconformity represented at C, fig. 1, that is to say, above the most marked unconformity of the whole section and one which represents the most profound break in the conditions of deposition.

(2) The occurrence of Cretaceous and Tertiary deposits at Martha's Vineyard, 50 miles south of Third Cliff, and of Tertiary deposits at Marshfield, seven miles south of Third Cliff, make it seem not unlikely that deposits of the same age once extended farther north, as well as farther inland, though subsequent erosion may have all but completed the removal of such deposits.

(3) The similarity of the material and the many points of similarity of sequence in these several places indicate the strong possibility that the Third Cliff beds are to be correlated with those farther south.

(4) The identity of plant remains offers the same possibility based on an independent line of evidence.

(5) The convergence of independent possibilities renders the following more than *possibilities:* they may be accepted as *probabilities:*

(*a*) The underlying yellow clay and the yellow and white sands are considered as probably upper Cretaceous. (*b*) The overlying dark sands and clays are probably Miocene though possibly Eocene or Oligocene.

Art. XXX.—*A Delicate Color Reaction for Copper, and a Microchemical Test for Zinc;* by Harold C. Bradley.

[From the Chemical Laboratory of the Yale Medical School.]

It has been known for a number of years that the extract of logwood-haematoxylin—would produce with copper salts a dark blue color of some intensity. One of the older and little used differential stains for tissues depended upon this reaction. The microtome section of tissue was immersed first in a copper solution, then washed and immersed again in a dilute solution of haematoxylin. Those portions of the tissue which fixed the copper would then be colored dark blue, while the rest of the tissue remained uncolored. In this way a stain is produced which will differentiate the cell nucleus from the surrounding cytoplasm. This same reaction was used by Herdman and Boyce* to demonstrate copper in the blood and tissues of the oyster, while Mendel and Bradley† made use of it in localizing the copper in the liver tissues of other marine molluscs. So far as we are aware, however, the reaction has never been used as a means of identifying small amounts of copper in solution, nor has it been realized of what extreme delicacy the reaction is susceptible.

Accordingly a number of trials were made with copper sulphate solutions of varying strengths, to determine within what limits the reaction was available for the detection of copper, and also how the reaction compared in delicacy with other well known tests for that element. Ferrocyanide, ammonium sulphide, potassium iodide and starch, are the reagents most commonly employed to detect small amounts of copper, and form some of the most delicate reactions of the laboratory. Potassium ferrocyanide gives, with dilute solutions of copper salts, a characteristic brown color, becoming indistinguishable from the color of the reagent when the copper solution contains less than 0·001 per cent of the metal. With starch paste and potassium iodide the reaction is slightly more delicate—cuprous iodide and starch iodide of characteristic deep blue being formed—but reaches its limit when the copper solution contains less than 0·001 per cent of the metal. On the other hand, the haematoxylin reaction is at its best in just such dilutions and will serve to recognize copper in solutions of much greater attenuation. The following table shows roughly the comparative delicacy of these reactions:

Reagent	0·01% Cu	0·001%	0.0001%	0·00001%	0·000001%	0·0000001%
Ferrocyanide	brown	brown	?	----	----	----
KI + starch	blue	blue	blue	----	----	----
Haematoxylin	blue	blue	blue	blue	blue	blue

* Herdman and Boyce: Report of the Thompson-Bates Laboratories, Liverpool, ii, 1899.

† Mendel and Bradley: American Journal of Physiology, xiv, 313, 1905.

That is, while under the most favorable conditions ferrocyanide of copper is formed visibly in solutions of one part copper in 100,000 parts of water, blue starch iodide in solutions of one part copper in 1,000,000 parts of water, the copper-haematoxylin compound is distinctly recognizable in solutions of one part of copper in 1,000,000,000 parts of water. This is, we believe, one of the most delicate reactions known, chemical or physical, and is comparable with the physiological effects of copper salts on certain algae, with the catalytic effect of copper in certain oxidations, and with the reactions for detecting radio-active bodies of extreme dilution. It is a thousand times more delicate than the ferrocyanide test for copper.

The possibilities for the use of such a reaction as a qualitative test for copper in drinking water from reservoirs treated with copper sulphate to destroy algae, is at once apparent. Whether the reaction can be applied directly to the proximate analyses of drinking waters, what the conditions for optimum results are, and what the intensely blue copper compound is, are problems still to be worked out.

Zinc.—In carrying out some investigations on the normal presence and distribution of zinc in certain marine gastropods,* the difficulty of recognizing definitely small amounts of that metal in tissue ash containing relatively large amounts of copper, iron, calcium, and phosphoric acid, was found to be very great. Zinc forms practically no colored compounds by which it may be identified in such a mixture, and the ordinary processes of separation are tedious and unsatisfactory. The desirability of finding some rapid and reliable test for zinc led to a thorough canvassing of the less common laboratory reagents for precipitating that metal, and the finding of a microchemical test which proved to be adequate in every way. The reaction is by no means a new one, but its possibilities as a reliable test for zinc seem to have been overlooked.

A moderately concentrated solution of a zinc salt when treated with sodium nitroprusside throws down a salmon-pink precipitate of zinc nitroprusside, fairly insoluble in cold water, much less so in hot. The characteristic feature of this precipitate is its definite and readily identified crystal form. All the other insoluble nitroprussides of the heavy metals are amorphous, slimy precipitates resembling the ferrocyanides in general physical properties. Thus even in a mixture of several metallic salts, such as copper, silver, cobalt, zinc, etc., the zinc nitroprusside can be recognized under the microscope by the presence of its characteristic crystals in the amorphous mass of the other nitroprussides. In performing the test, it is desirable to have the solution of the salts fairly concentrated—about

* Bradley: Science, 1903, xix, p. 196.

10 per cent strength is convenient—and to remove the copper by H_2S. In such solutions of tissue ash as were used in our experiments, copper was first removed and the filtrate containing iron, calcium, phosphoric acid, etc., concentrated to small bulk. A drop of this solution placed on a microscope slide and digested with a drop of the freshly prepared nitroprusside solution, deposited on cooling the rectangular plates and prisms of the zinc salt when that metal was present in such minute amounts that the ordinary methods of separation and identification failed to show it definitely, or required the ashing of large amounts of the original material. For example, by this method zinc was detected readily in the blood of certain molluscs in a few minutes, while by the ordinary methods of separation and analysis—the basic acetate method, or better, the precipitation of the metal as sulphide from a formic acid solution—many hours are required to ash sufficient material and carry through the steps of the analysis.

ART. XXXI.—*The Elimination and Alkalimetric Estimation of Silicon Fluoride in the Analysis of Fluorides;* by ALBERT HILEMAN.

[Contributions from the Kent Chemical Laboratory of Yale Univ. cxlviii.]

THE errors of the processes for the determination of fluorine, in which that element is eliminated as silicon fluoride to be subsequently estimated volumetrically, naturally fall into two categories. First, there are those errors which are due to imperfect elimination and collection of the silicon fluoride from the decomposition flask, and, secondly, there are the errors of the titration processes. For the present purpose it will be most convenient to consider the latter class of errors first.

The Process of Titration.

As has been indicated, methods have been used for the determination, by volumetric processes, of silicon fluoride. First, the method of Penfield, which depends upon the collection of the silicon fluoride in an alcoholic solution of potassium chloride and the titration, without removal of the precipitated potassium fluosilicate, of the hydrochloric acid set free. It is assumed that in the alcoholic solution the fluosilicic acid and potassium fluosilicate are not appreciably hydrolized and that ammonia may exactly neutralize the hydrochloric acid without attacking the precipitated potassium fluosilicate. Cochineal is used as the indicator.

$$3SiF_4 + 4H_2O + 4KCl = 2K_2SiF_6 + SiO_4H_4 + 4HCl$$
$$NH_4OH + HCl = NH_4Cl + H_2O$$

The second method of titrating the silicon fluoride, resembling that of Penfield, except that standard sodium hydroxide or potassium hydroxide is employed instead of ammonium hydroxide in titrating the free acid, which is the method of Bullnheimer* and used by Treadwell and Koch,† involves very similar reactions.

$$3SiF_4 + 4H_2O + 4KCl = K_2SiF_6 + SiO_4H_4 + 4HCl$$
$$NaOH + HCl = NaCl + H_2O$$

The third method, that of Offerman,‡ differs from the preceding methods in this respect, that the silicon fluoride is allowed to act upon water and the fluosilicic acid and hydrofluoric acid thus formed are acted upon by standard potassium

* Zeitschr. Angew. Chem. 101, 1901.
† Zeitschr. Anal. Chem. xliii, 444, 1904.
‡ Zeitschr. Angew. Chem. 615, 1890.

hydroxide to the point of complete hydrolysis of the fluosilicate to the condition of a fluoride.

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + SiO_4H_4$$
$$H_2SiF_6 + 6KOH = 6KF + SiO_4H_4 + 2H_2O.$$

According to this process the amount of the standard alkali used is three times as great as that used to the end reaction of the preceding process. According to a fourth method advocated by Tammann* and useful when fluorides are to be determined in the presence of carbonates, the potassium fluosilicate is precipitated and separated with precautions and titrated by itself with standard potassium hydroxide to the point of formation of potassium fluoride and silicic acid.

$$K_2SiF_6 + 4KOH = 6KF + SiO_4H_4$$

This process is essentially similar to the second process so far as concerns the reaction involved, but only two units of the alkali used for neutralization are of the standard alkali. For the present purpose therefore, it will suffice to compare the first three methods as to the degree of agreement between individual results, and between the averages and the processes. For this purpose measured portions of a solution of fluosilicic acid were treated according to the methods described and the results are recorded in the following table:

TABLE I.

Titration in Alcoholic Solution.

	(According to Penfield.)		(According to Bullnheimer.)		
H_2SiF_6 cm_3.	Standard NH_4OH cm_3.	Standard KOH cm_3.	Standard NaOH cm_3.	Fluorine Found. grm.	Average. grm.
25	7·3	----	----	0·1433	
25	7·3	----	----	0·1433	
25	7·27	----	----	0·1426	0·1428
25	7·23	----	----	0·1429	
25	7·29	----	----	0·1431	
25	----	10·67	----	0·1412	
25	----	10·72	----	0·1419	
25	----	10·64	----	0·1408	0·1411
25	----	10·67	----	0·1412	
25	----	10·60	----	0·1403	
25	----	----	9·11	0·1416	
25	----	----	9·12	0·1418	
25	----	----	9·07	0·1410	0·1415
25	----	----	9·10	0·1414	
25	----	----	9·12	0·1418	

* Zeitschr. Anal. Chem. xxiv, 328, 1885.

The differences between the amounts of fluorine indicated by the individual determinations in any one of these processes are generally slight. The averages of the determinations by potassium hydroxide and sodium hydroxide are very close together, being 0·1411 grams and 0·1415 grams of fluorine. The average of the titrations by ammonium hydroxide is a little higher, namely, 0·1428 grams. That the differences between these averages are due to gradual variations in the reading tint is shown by a comparison of three titrations as nearly simultaneous as possible, in which the greatest care was taken to bring all to the same tint at the final reading.

TABLE II.

Comparison of Simultaneous Titrations in Alcoholic Solution.

	Solution used. cm_3.	Fluorine Found. grm.
Titration by NH_4OH	7·2	0·1414
Titration by KOH	10·71	0·1418
Titration by NaOH	9·13	0·1419

So it appears that the results obtained are practically the same by the three processes of neutralization applied to a solution of fluosilicic acid. But it is to be observed that all are possibly subject to a common and constant error due to the presence of hydrofluoric as well as fluosilicic acid. If the former acid is present it tends to raise the apparent value of the latter.

With these results of titrations in alcoholic solution are to be compared the results obtained by the method of titration in the water solution (in which the fluosilicate is completely converted to fluoride), recorded in the following table:

TABLE III.

Titrations of Fluosilicic Acid in Water Solution.
(According to Offerman.)

H_2SiF_6 Taken cm_3.	Standard KOH cm_3.	Standard 1NaOH cm_3.	Fluorine Found. grm.	Average. grm.
25	30·9	----	0·1358	
25	30·8	----	0·1353	0·1355
25	30·9	----	0·1358	
25	30·79	----	0·1353	
25	----	26·2	0·1357	
25	----	26·15	0·1355	
25	----	26·25	0·1360	0·1358
25	----	26·2	0·1357	
25	----	26·13	0·1354	
25	----	26·14	0·1354	

It is obvious that the process of titrating fluosilicic acid in water solution yields uniform indications, both with potassium hydroxide and sodium hydroxide, but that the values for fluorine are very much below those of the titrations in alcoholic solution. And this would be the case if the solution of fluosilicic acid contains hydrofluoric acid as is natural.

In the analytical process in which silicon fluoride is passed into the alcoholic solution of potassium chloride the formation of hydrofluoric acid is likely to be at a minimum and so the titration of the hydrochloric acid set free in this metathesis should indicate closely the actual amount of fluorine present. If, however, the silicon fluoride is passed into water instead of into this alcoholic solution of potassium chloride, it is necessary to titrate together the products of action, fluosilicic acid and hydrofluoric acid, to the point of formation of the alkali fluoride, in order that the indication may be correct.

The action of ammonium hydroxide upon fluosilicic acid in water solution proves to be comparable with that of sodium hydroxide, and inferentially with that of potassium hydroxide, though the hydrolysis of the fluosilicate appears to be not quite so complete. In the table are given the results of comparative titrations.

TABLE IV.

H_2SiF_6 taken cm³.	NH_4OH [1cm³=0·006547] cm³.	Fluorine found by NH_4OH grm.	Fluorine found by NaOH grm.
25	31·04	0·2030	0·2057
25	31·00	0·2030	0·2057
10	12·39	0·0811	0·0823
10	12·42	0·0816	0·0823
10	12·42	0·0811	0·0823

The following expression represents the reaction :

$$6NH_4OH + H_2SiF_6 = 6NH_4F + Si(OH)_4 + 2H_2O$$

When silicon fluoride is passed into water containing ammonium hydroxide, as is suggested in Liversidge's method for the analysis of fluorides, it is obvious that nearly complete hydrolysis must take place, with formation of silicic acid precipitated or colloidal, according to the equation

$$SiF_4 + 4NH_2OH = 4NH_4F + Si(OH)_4.$$

According to Liversidge, potassium fluosilicate may be thrown down by addition of potassium chloride and alcohol, after dissolving the precipitated silica by heating the ammoniacal liquid. In my experience, it has never been possible to thus dissolve all the silica, and the precipitate obtained by adding potassium chloride, with or without alcohol, appears to be

* Chem. News xxiv, 266.

silica thrown out of its colloidal solution by addition of the electrolyte.

The Elimination of Silicon Fluoride.

As to the sources of error due to imperfect elimination, and collection, of silicon fluoride, we have the testimony of the several investigators already quoted. The importance of using the fluoride in the finest state of division, of having the sulphuric acid of highest strength, of properly absorbing the vapors of sulphuric acid evolved from the decomposition flask, and of using quartz for the silicon dioxide in the decomposition flask, have all been emphasized. Many forms of apparatus have been employed and the results have varied widely, errors of from 0·0010 grams to 0·0050 grams in the determination of fluorine by absorption and weighing of silicon fluoride being not uncommon.

At the outset of the work to be described, an investigation was made as to the limit of error likely to occur in the use of simple apparatus and sulphuric acid, prepared by heating to the fuming point, for about a half hour. The silicon fluoride evolved was estimated by absorption in an alcoholic solution of potassium chloride following the method of Penfield,* and the hydrochloric acid set free was estimated by standard potassium hydroxide.

The apparatus employed consisted of the following parts: First, there was an apparatus for purifying the air current by passing it through a sulphuric acid wash bottle and two large drying cylinders containing fused calcium chloride at the bottom and soda lime at the top; second, a 100^{cm^3} decomposition flask provided with a doubly perforated rubber stopper, through which passed a glass tube from the drying cylinders to the bottom of the flask, while another tube, leading from this decomposition flask, was joined to a large empty U-tube intended to condense any sulphuric acid which might be carried from the decomposition flask. Third, connected with the outer limb of the U-tube for condensing sulphuric acid was an absorption system similar to that described by Burk.† It consisted of a test tube 34^{cm} in length and 2^{cm} in diameter, containing a few cm^3 of mercury into which extended a delivery tube with a capillary opening. The test tube was placed at an angle to diminish the pressure throughout the system.

Before making a determination, the apparatus was first carefully dried. The absorption tube was filled with a saturated solution of potassium chloride in 50 per cent alcohol, and the material to be analyzed, weighed on a watch glass, was trans-

* Am. Chem. Jour., i, 27.

† Jour. Am. Chem. Soc. xxiii, 825 (1901).

ferred to the decomposition flask through a funnel with a short neck. To the material were added fifteen times its weight of ignited quartz sand and 50$^{cm^3}$ of sulphuric acid which had been previously heated strongly and cooled in a desiccator. To an iron plate supporting the decomposition flask, heat was applied by a burner and regulated so that a flask of sulphuric acid placed where it received the same amount of heat as the decomposition flask should have a temperature of between 150° and 160°. During the heating a slow current of air was passed through the apparatus. In the reaction in the decomposition flask hydrofluoric acid was generated which acting on the silica formed silicon fluoride. In the absorption tubes silicon fluoride acted on water according to the following equation:

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + SiO_4H_4$$

In the presence of potassium chloride and alcohol the fluosilicic acid was precipitated as potassium fluosilicate, and a corresponding amount of hydrochloric acid set free.

$$H_2SiF_6 + KCl = K_2SiF_6 + 2HCl.$$

The hydrochloric acid was then titrated with a standard potassium hydroxide solution, using cochineal as an indicator.

A series of experiments, carried out in the manner described, was made with ordinary pulverized fluorite. The heating was continued in every case above the time limit of two hours. All gas bubbles had disappeared from the acid mixture, which fact, according to Fresenius* and Offerman,† shows that the decomposition is complete.

The time required to decompose fluorite is stated by Penfield to be two hours for 0·2 to 1·0 grams; by Fresenius two hours for 0·1 gram and four hours for 1·0 gram.

TABLE V.

	CaF_2 grams.	Silica grams.	KOH cm^3. ($1^{cm^3} = 0{\cdot}01045F.$)	Theory Fluorine grams.	Found Fluorine grams.	Error Fluorine grams.
1.	0·5000	7·0	22·7	0·2432	0·2372	−0·0060
2.	0·5000	7·0	22·56	0·2432	0·2357	−0·0075
3.	0·5000	7·0	22·7	0·2432	0·2372	−0·0060
4.	0·5000	7·0	23·15	0·2432	0·2419	−0·0013
5.	0·5000	7·0	22·4	0·2432	0·2340	−0·0092
6.	0·5000	7·0	21·7	0·2432	0·2277	−0·0155
7.	0·5000	7·0	22·	0·2432	0·2299	−0·0133
8.	0·5000	7·0	21·7	0·2432	0·2267	−0·0165
9.	0·5000	7·0	22·5	0·2432	0·2351	−0·0081

* Zeitschr. Anal. Chem., vi, 190. † Loc. cit.

The cause of the variation in the results, and of the occasionally very large errors in the above series of experiments, was not apparent at the time when the experiments were made, but reference will be made to this later.

Crystals of fluorite, perfectly clear and of a pale green color, were next tried. The powdered mineral on treatment with sulphuric acid yielded the theoretical amount of calcium sulphate.

TABLE VI.

	CaF_2 grams.	KOH cm^3	Fluorine Theory grams.	Fluorine Found grams.	Flourine Error grams.	Time hours.	Temperature.
			(1^{cm} = 0·01045 Fluorine.)				
1.	0·5000	21·77	0·2432	0·2274	−0·0158	6	150°
2.	0·5000	22·	0·2432	0·2299	−0·0133	6	160°
3.	0·5000	31·77	0·2432	0·2274	−0·0158	3·25	
4.	0·5000	23·6	0·2432	0·2466	−0·0034	6	
5.	0·5000	22·15	0·2432	0·2314	−0·0118	6	180°
6.	0·5000	22·19	0·2432	0·2318	−0·0114	6	
7.	0·5000	19·37	0·2432	0·2014	−0·0418	6	
8.	0·5000	16·2	0·2432	0·1692	−0·0740	3	
9.	0·5000	22·2	0·2432	0·2325	−0·0107		boiling.
10.	0·5000	21·25	0·2432	0·2220	−0·0212		

In experiment (1) above, the heating was continued for six hours at 150–160°. In experiment (2) the powdered mineral was fused with sodium carbonate and the mixture transferred to the decomposition flask. In experiments 2–8 above, the temperature was raised as high as 180°, while the empty U-tube was immersed in a freezing mixture of salt and ice. Blank determinations showed that some sulphuric acid was carried over under these conditions. In experiments (9) and (10) the acid was heated to boiling and allowed to cool before the air current was passed through.

The effect of precipitated silica instead of quartz sand was next tried. In experiment (1) the silica was air dried; in (2) it was strongly ignited.

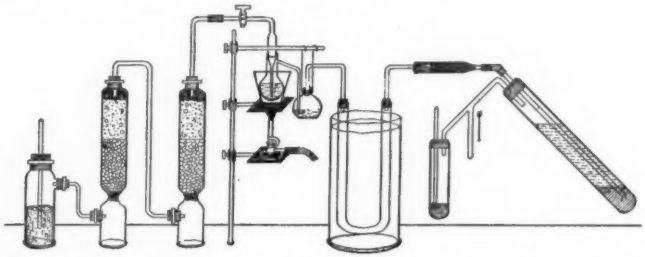
TABLE VII.

	CaF_2 grams.	Silica grams.	KOH cm^3	Theory Fluorine grams.	Found Fluorine grams.	Error Fluorine grams.
1.	0·5000	7·0	6·4	0·2432	0·0668	0·1764
2.	0·5000	7·0	21·2	0·2432	0·2215	0·0217

These experiments indicate that the small amount of water in the air dried silica may cause great deficiency in the fluorine found, and suggests the idea that even the amount of water produced in the reaction involving the sulphuric acid, the fluoride and silicon dioxide may be the occasion of trouble.

A Specially Devised Apparatus for use at High Temperatures.

Owing to the lack of success with the silicon fluoride processes in which the decomposition was effected at temperatures between 150°–160°, an attempt was made to devise a simple and convenient form of apparatus in which the acid mixture might be heated to boiling to facilitate the removal of the silicon fluoride to the absorption system.



After a number of experiments with this end in view the following model of apparatus was found to be the most satisfactory: a glass stopper, made by drawing out a glass tube 1^{cm} in diameter and sealing a small glass tube on each end, is ground into a 70^{cm^3} side neck flask. To one end is sealed a glass stop-cock. The other end extends to the bottom of the flask. The side neck is sealed to a Voit flask. The length of the tube between the two flasks is 17^{cm}, and it is bent at right angles, 12^{cm} from the Voit flask. The tube leading from the Voit flask enters a large empty U-tube through a rubber stopper. A tube from the other limb of the U-tube enters a trap loaded with phosphorus pentoxide. A rubber connection joins the trap with the delivery tube of the absorption apparatus described above. Connected with the absorption tube is a pressure regulator. This consists of a T-tube, one opening of which enters a test tube of mercury through a rubber stopper. Another perforation is closed with a glass tube which may be raised or lowered in the mercury. The third opening of the T leads to the aspirating pump.

Preparatory to making a determination the apparatus is carefully dried. The tip of the delivery tube is then placed beneath the surface of the mercury in the absorption tube and distilled water is added, care being taken that enough space remain for the rise in level when air bubbles are in the liquid. The pressure regulator is then connected with the absorption tube and adjusted so that a rise of pressure in the apparatus should be relieved but no appreciable vacuum created. The U-tube is then immersed in a vessel of cold water and connected with the trap. Next, the mineral, together with quartz powder

to about three times the weight of the fluorine present, is transferred to the decomposition flask. Next, enough sulphuric acid to seal the delivery tube from the side neck flask is introduced into the Voit flask. The two flasks are then tilted so that the acid should moisten the connecting tubes to the bend. About 40^{cm^3} of sulphuric acid and several capillary tubes 1^{mm} in diameter sealed 1^{cm} from an open end and at the other end* to prevent bumping, are added to the decomposition flask, and the stopper quickly replaced and sealed with a drop of sulphuric acid. The acid used above had been boiled for half an hour and a current of dry air passed through on cooling. A thin strip of asbestus is wrapped about the neck of the flask, and the stop-cock having been closed, the bulb is heated in a radiator whose top is covered with a sheet of asbestus matting.

When heat is applied in the process, bubbles of gas are given off, the solid material rises to the surface, and during the course of the heating an oily film gathers on the upper part of the flask and in the delivery tube. On boiling, this film is replaced by a white deposit which recedes before the acid vapors. The success of the determination depends, as was found, on the removal of this deposit. When the acid vapors have penetrated the length of the tube leaving it clear or translucent, the decomposition is complete, and the stop-cock having been opened, the side neck flask is cooled to about 75°. A current of purified air is drawn through the apparatus, slowly at first and then more rapidly. About six liters are necessary to remove the last trace of silicon fluoride.

Daniels'† suggestion that the deposit mentioned above is a polymer of SiF_4 appears unwarranted. It seems more probable that this is a product of partial hydrolysis of silicon fluoride by the action of water generated in the action of sulphuric acide on the fluoride, as suggested above, the process of forming and hydrolyzing silicon fluoride being repeated until the water is finally absorbed in the cold acid of the Voit flask.

If it happens that the acid mixture bumps before the decomposition is complete, some of the deposit may become dislodged from the tube and remain undecomposed in the Voit flask. Bumping also renders it difficult to boil the acid vapors through the delivery tube. On this account the tube between the two flasks should be as short as is practicable. Unsatisfactory results were obtained when the tube was about one-half longer than the dimensions given above. If the acid tends to suck back from the Voit flask, it is arrested by opening the stop-cock for a moment to relieve the vacuum. If, at this point of the experiment, the pressure regulator should not be adjusted properly, acid vapors would be drawn through the

* Scudder, J. Am. Chem. Soc., xxv, p. 113.

† Zeitschr. Anorg. Chem. xxxviii, 257.

apparatus into the absorption tube. The decomposition is ended in fifteen to forty minutes. The delivery tube is washed and the absorption solution transferred to a flask and titrated with sodium hydroxide* from an alkali burette, with phenolphthalein as an indicator, according to the method of Offerman, the third method referred to above.

$$H_2SiF_6 + 6NaOH = 6NaF + Si(OH)_4 + 2H_2O$$

The following series of results was obtained according to the method outlined above.

TABLE VIII.

	CaF_2 grams.	Quartz grams.	Na_2OH cm. ($1^{cm_3} = 0{\cdot}005123F.$)	Theory Fluorine grms.	Found Fluorine grms.	Error Fluorine grms.
1.	0·3000	0·4	28·2	0·1459	0·1444	−0·0015
2.	0·3000	0·4	28·35	0·1459	0·1452	−0·0007
3.	0·3000	0·4	28·34	0·1459	0·1451	−0·0008
4.	0·3000	0·4	23·5	0·1215	0·1203	−0·0012
5.	0·3000	0·4	28 3	0·1459	0·1419	−0·0010
6.	0·3000	0·4	28·37	0·1459	0·1453	— ·0006
	NaF.					
7.	0·3000	0·4	26·2	0·1356	0·1342	−0·0012
8.	0·3000	0·4	26·44	0·1356	0·1355	−0·0001
9.	0·3000	0·4	26·46	0·1356	0·1356	— ·0000
10.	0·3000	0·4	26·3	0·1356	0·1347	−0·0009
11.	0·3000	0·4	26·34	0·1356	0·1349	−0·0007
12.	0·3000	0·4	26·3	0·1356	0·1347	−0·0009
		Ignited Silicic acid				
13.	0·3000	0·4	26·29	0·1356	0·1346	−0·0010
		Quartz				
14.	0·3000	0·4	26·3	0·1356	0·1347	−0·0009
	Ca = 40·1		Na = 23·04	F = 19	(error	−0·0008)

With the apparatus described above, in which the sulphuric acid in the decomposition flask may be boiled, the silicon fluoride formed passes rapidly to the absorption system, other products of partial hydrolysis of silicon fluoride formed in the flask or tube are ultimately reconverted to silicon fluoride, and regular results of a fair degree of accuracy are obtained. In all the experiments above except (6) and (14) phosphorus pentoxide, about 2·0 grams was introduced into the decomposition flask, the purpose being to retain water formed in the reaction. The results of the experiments specifically mentioned show, however, that phosphorus pentoxide in the flask is not essential.

In three blank experiments, where the acid in the decomposition flask was heated to boiling, amounts of acid in each case equivalent to 0·0002 grams of fluorine were found in the absorption solution; the above results therefore are subject to this trifling error.

*Kuster, Zeitschr. Anorg. Chem. xli, 475.

ART. XXXII.—*Note on the Actual Drop of Pressure in the Fog Chamber;* by C. BARUS.

1. THE apparatus for condensation, as I have endeavored to use it, consists of a fog chamber in communication with a vacuum chamber through a wide stop-cock. The former may be put in connection with the filter; the latter with the air pump. It is necessary to wait between operations, all observing being done at the same temperature. In this case the isothermal value of the drop of pressure cannot be read off at the fog chamber (as I supposed it could, nearly), however rapidly the cock is closed after exhaustion; but it may be computed from the initial pressures of the isolated fog and vacuum chambers before exhaustion, and the final pressure when the vessels are in communication after exhaustion, if the ratio of volumes of the vessels is known.

2. Let v be the volume of the fog chamber, V the volume of the vacuum chamber, k/c the ratio of specific heats of the gas (moist or dry as required); let p, v, τ, ρ, denote its pressure, volume, absolute temperature and density under conditions given by the subscripts. It will be convenient to refer to the vacuum chamber by the same symbols with *accents*. Hence the thermal states will be for dry air.

	For the Fog chamber.			For the Vacuum chamber.		
Initially	p	τ	ρ	p'	$\tau'=\tau$	ρ'
Adiabatically (alone)	p_1	τ_1	ρ_1	$p_1'=p_1$	τ_1'	ρ_1'
Isothermally (alone)	p_2	$\tau_2=\tau$	$\rho_2=\rho_1$	p_2'	$\tau_2'=\tau$	$\rho_2'=\rho_1'$
Isothermally (together)	p_3	$\tau_3=\tau$	ρ_3	$p_3'=p_3$	$\tau_3'=\tau_3$	$\rho_3'=\rho_3$

The equations describing the transformations are (for dry air)

$$(\tau/\tau_1)=(p/p_1)^{(k-c)/k}\quad(\tau/\tau_1')=(p'/p_1)^{(k-c)/k} \tag{1}$$

$$\begin{aligned} p &= R\rho\tau & p' &= R\rho'\tau \\ p_1 &= R\rho_1\tau_1 & p'_1 &= R\rho'_1\tau_1' \\ p_2 &= R\rho_1\tau & p'_2 &= R\rho'_1\tau \text{ or} \\ p_3 &= R\rho_3\tau & p_2/p'_2 &= \rho_2/\rho'_2 \end{aligned} \tag{2}$$

$$\rho v+\rho' V=\rho_1 v+\rho'_1 V=\rho_2 v+\rho'_2 V=\rho_3(v+V) \tag{3}$$

From these one may deduce relative to the value of p_1

$$p_1^{c/k}=\frac{p_3(1+v/V)}{p'^{(k-c)/k}+(v/V)\,p^{(k-c)/k}} \tag{4}$$

$$p'_2+p_2\,.\,v/V=p_3(1+v/V) \tag{5}$$

where p, p', p_2, are observable with certainty. While equation (5) is variously useful in checking the results, it does not admit of the individual determination of p_2 and p'_2. For this purpose, however, the equations (1) and the second and third of group (2) are available, with the results (for dry air)

$$p_2 = p^{(k-c)/k} p_1^{c/k} \qquad p'_2 = p'^{(k-c)/k} p_1^{c/k} \qquad (6)$$

as $p_1^{c/k}$ is given in equation (4).

Using these equations the data of the following table were computed in connection with incidental results tested for the purpose.

TABLE.—Pressures p (cm) and temperatures t (°C.) at the fog and vacuum chambers, the latter marked with an accent.

p	p'	p_2	p'_1*	p_1	p_2	p'_2	p''_1†	t_1	t'_1
76	43·5	45·5	47·9	45·7	52·9	45·0	45·6	—20·2	24·3
76	51·5	52·5	54·3	52·4	58·3	52·1	...	— 9 9	21·5
76	59·5	59·7	62-2	59·4	63·8	59·4	...	— ·2	20·

3. The pressures of the table are computed for dry air throughout and if charted in terms of p', graphically, are found to lie very nearly on straight lines. The results of the table are very important. In the first place it will be seen not only that isothermal pressures or nearly isothermal pressures are not observed, but that the effect of the vacuum chamber is preponderating. Thus the pressure at the latter p_1'', read off as soon as possible and nominally adiabatic, is within one millimeter of p_2. Similarly the computed adiabatic pressure p_1 is within a few millimeters of p_1'' and p_2. It follows, therefore, that even an approach to isothermal pressure, to say nothing of adiabatic pressure, cannot be observed at the fog chamber at all; or that before the exhaust cock can be closed again the vacuum chamber has practically regained its isothermal pressure by cooling and that the fog chamber is further exhausted by a corresponding amount.

The pressure $p_1' = p''_2$ observed under isothermal conditions‡ at the fog chamber, exceeds p_1 (computed) by about $1{\cdot}9^{cm}$ on the average, which might be regarded as the average vapor pressure of water at the temperature at which the observation was made. Leaving this for further consideration, the final result of importance is the following: p_2 the computed isothermal pressure in the closed fog chamber is from 2 to 5^{cm} above the (nominally) isothermal pressure $p_1' = p_2$ observed: and correspondingly more than this above the common isothermal

* Observed as soon as possible after exhaustion at the closed fog chamber.

† Observed as soon as possible after exhaustion at the vacuum chamber, stop cock closed at once after exhaustion.

‡ This pressure varies but slightly.

value p_3 usually taken. For the region in which colloidal nuclei lie the correction will be 6 to 8^{cm}. Now this is in excess of the difference between the pressure regions in which Wilson's data for colloidal nuclei, as reduced elsewhere,* and the region in which my own data as summarised heretofore, would lie.

In other words, the data in my large coronal apparatus lie in regions of exhaustion at least as moderate as those observed in Wilson's small apparatus; or the two types of apparatus comparing efficiency if the drop of pressure taken is in my case not the (apparent) experimental value, but that deduced for the computed isothermal pressure p_2 of the fog chamber as above explained.

4. For the case of air saturated with water vapor in both chambers, all pressures must be reduced by the corresponding vapor pressure, π of water, except p'_1, when the vapor is slightly superheated. Apart from this, the equations take the above form, though special computation is needed, since a different initial pressure $(p-\pi)$ enters. So computed, the relation between the observed drop of pressure $p-p_3$ and the computed drop $p-p_2$ was found to be

$$(p-p_3)/(p-p_2) = \cdot 775$$

and very nearly constant with the pressure interval involved. The conclusions as to efficiency are like the above.

The fact that a limit has been reached for condensations, within the given type of fog chamber, may be considered as proved, apart from comparison with Wilson's results, since for a successively increasing drop of pressure $(p-p_3)$, no matter whether the nuclei are relatively large like the ions or relatively small like the colloidal nuclei, the same terminal corona is eventually reached in both instances. Higher exhaustions are thereafter powerless. Finally, since the colloidal nuclei in case of dust-free air saturated with alcohol vapor† are larger than in case of water vapor (caet. par.), these nuclei must probably be associated with the saturated vapor, the gas being but secondarily in question.

Brown University, Providence, R. I.

* Presidential address; Physical Review, xxii, 1606, p. 107.

† This Journal, August.

Art. XXXIII.—*On a New Method for Standardizing the Coronas of Cloudy Condensation;* by C. Barus.

Assuming that for ions produced within the fog chamber the rate of decay in the lapse of time t is as the square of the number, or that $1/n - 1/n' = b(t-t')$ where b is constant, a few incidental attempts were made to compute b, when the number, n, of nuclei (ions) is expressed in thousands per cubic centimeter. The table gives an example of such results, obtained by exhausting the fog chamber at a stated time t, after the removal of radium. If the drop in pressure is *below* the coronal fog limit of air, precipitation takes place on ions, only.

Table.—Decay curve. Nucleation observed and computed. $b = \cdot0024$ relative to $n \times 10^{-3}$. Radium suddenly removed from top of fog chamber (glass) and exhaustion made t sec. thereafter. $\delta p = 23^{cm}$ (below the coronal fog limit of dust free air). $s/30$ (nearly) angular diameter of coronas.

t sec.	s cm.	(observed) $n \times 10^{-3}$.	(Computed for $b = \cdot0024$) $n \times 10^{-3}$.
0	5·9	67	67
5	5·0	41	37
10	4·6	32	26
15	4·0	21	20
20	3·5	15	16
30	3·3	12	12
50	2·9	7	7
120	1·7	2	3
∞	1·0	1	--

For the first five seconds $b = \cdot0019$; for the first fifteen seconds $b = \cdot0022$; etc., values obtained ranging from ·002 to ·003. This is larger than the corresponding electrical datum, say ·0014, when n is given in thousands. Decay is more rapid than the equation warrants. Initial coronas are too large, final coronas too small, in spite of the presence of air nuclei, the number of which should be deducted, at least in part. Other experiments show similar coefficients. Naturally the present method for b is much inferior to the electrical method, even if the two coefficients are identical; and the b here is obtained under possible complications with the larger gradations of the colloidal nuclei of dust free air, though these are probably inefficient.

If the values of $1/n$ be inserted the curves should be linear since $1/n = 1/n_0 + bt$ where t is the time dated since the occurrence of n_0. The line passing through the observations at 5, 30, 50 seconds is best adapted to represent the results, and

from it $b = \cdot 0024$ (n in thousands of nuclei per cubic centimeter) may be roughly assumed. These computed values of n are given in the table. Shown in a chart, they are too low initially and too high finally, even if the air value is quite ignored; but the constant probably reproduces the true conditions better than the observation, remembering that the initial corona ($t = 0$) is not quite invariable.

A very important consequence may be deduced from these results. The equations specified may be written $n_0 = (n_0/n - 1)bt$. Hence if the ratio of nucleations or of ions is known (for instance by my method of geometric sequences), n_0/n is given, and the absolute value of n_0 may be computed if b is known. Now if b for the case of ions may be taken as identical with the value found in electrical experiments, where $b = \cdot 0014$ roughly and relative to ionization in thousands,

$$bn_0 = \cdot 0014 n_0'$$

where n_0' is the true nucleation. Thus in the table $b = \cdot 0024$, $n_0 = 67 \cdot 5$; therefore $n_0' = (\cdot 0024/\cdot 0014)\, n_0$ or 115,000 nuclei per cubic centimeter, instead of 67,500 for the initial corona. Quite generally if n_0/n and b are determined from purely coronal measurements

$$b \,/\, \cdot 0014$$

is the reduction factor for all the relative nucleations to absolute value.

Another important consequence may be drawn: If the coefficient is known from direct experiments, it will then be possible to standardize the residual curve (depressed asymptote) leading to the terminal corona, corresponding to groups of nuclei of different sizes occurring together.

Moreover, in any such curve, let the ordinates denote the computed number of ions, the abscissas denote the observed number of *efficient* nuclei, being the colloidal nuclei and ions occurring together in the course of a stated time. Then the curve gives an indication of the distribution of the precipitated water on the two groups of nuclei different in size and present in different proportions, for the given supersaturation. Experiments of this kind are of the highest importance and the present cursory treatment is admitted provisionally in view of a restandardization of the coronas of cloudy condensation which the variety of results since obtained has made necessary.

Brown University, Providence, R. I.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *Barium Sub-oxide and the Preparation of Metallic Barium.*—According to Winkler, magnesium reduces the alkaline earth oxides, but he was unable to isolate the metals from the resulting mixtures. Guntz has now repeated Winkler's experiment with barium oxide and magnesium in a vacuum at a high temperature with the expectation of collecting the metallic barium by distillation. It was found, however, that when the calculated quantities of the substances were thus treated at about 1100°, approximately one-half of the magnesium distilled off together with traces of barium. Upon examination of the residue it appeared that a sub-oxide of barium, Ba_2O, had been produced. This forms a black fritted mass, the properties of which are similar to those of metallic barium, since it decomposes water, gives Ba_3N_2 with nitrogen at a red heat and at the same temperature yields BaH_2.

When aluminium, a non-volatile metal, was used in place of magnesium in the experiment mentioned above, it was found that crystallized barium of 98·8 per cent purity was obtained at once at near 1200°, and by a second distillation in a vacuum it was obtained absolutely pure. This new method applies equally well to strontium and furnishes an easy means of obtaining these metals, which, up to the present time, have been so difficult to prepare.—*Comptes Rendus*, cxliii, 339. H. L. W.

2. *The Thermal Formation of Nitric Oxide and Ozone in Moving Gases.*—Franz Fischer and Hans Marx have made the interesting observation that ozone, as well as hydrogen peroxide and nitric oxide, may be obtained by burning hydrogen in air or oxygen by the use of a rapid current of the oxidizing gas, as a jet blown through the hydrogen flame. It has been previously known that suddenly cooling the hydrogen flame in other ways gives nitric oxide and hydrogen peroxide, but the formation of ozone from this source is new. They have found also the previously unknown fact that a rapid current of air blown over the glowing Nernst pencil gives ozone in addition to nitric oxide, and it appears that the proportion of ozone increases, in its relation to the nitric oxide, as the rapidity of the current of air increases. Quantitative results have not yet been obtained, but it seems possible to produce in this way enough ozone so that the nitrogen peroxide produced at the same time, when led into water or sulphuric acid, will yield no nitrous acid, but nitric acid exclusively.—*Berichte*, xlix, 2557. H. L. W.

3. *The Action upon Carbon of Oxygen, Carbon Dioxide and Steam.*—It has been found by P. Farup that, under the same conditions of experiment, water vapor and carbon dioxide act upon solid carbon at 850° C. with the same speed, while oxygen acts at this speed at about 450°. According to the temperature-coefficient

of the oxygen reaction between 450 and 500°, it is calculated that the speed of this reaction at 850° is 3×10^6 times as great as that of the carbon dioxide and water vapor reactions. From results obtained by Nernst and v. Wartenberg in regard to the dissociation of water vapor and carbon dioxide, it appears that oxygen at atmospheric pressure and 850° has a concentration about $0{\cdot}7 \times 10^6$ times as great as in water vapor and carbon dioxide at the same pressure and temperature; hence it appears that there is a connection between their dissociation and rate of action upon carbon. —*Zeitschr. anorgan. Chem.*, l, 276. H. L. W.

4. *The Combustion of Halogen Compounds.*—In determining carbon and hydrogen in substances containing halogens, CHARLES J. ROBINSON uses a cylinder of copper gauze filled with lead chromate in the combustion-tube. The cylinder is 6 or 7 cm. long and its copper parts are oxidized before use. The lead chromate is thus kept from contact with the glass. Some analyses are given showing satisfactory results by the use of this device with chlorine and bromine compounds, but no results are given for compounds containing iodine. Strange to say, the author recommends the use of the same device for nitrogen combustions, and gives a satisfactory result here also. It would be expected that oxygen would escape from the hot lead chromate and contaminate the nitrogen produced. H. L. W.

5. *Introduction to General Inorganic Chemistry*, by ALEXANDER SMITH. 8vo, pp. 780. New York, 1906 (The Century Co.).—This text-book contains many excellent features and it is a very interesting work for a teacher of chemistry to read. The author has wisely made the elucidation of theory the main feature of the book, but an ample amount of facts is included for the purpose in view. The clear and able treatment of the theories by basing them upon facts is noteworthy. The book is intended for the use of beginners in college courses. It is a more thorough and difficult book than those generally used, but this feature may be considered a favorable one. It may be added that the subject is treated from the most modern point of view, but without giving undue prominence to the newer theories. H. L. W.

6. *A First Course in Physics;* by ROBERT ANDREWS MILLIKAN and HENRY GORDON GALE. Pp. v, 488, with 494 figures. New York, 1906 (Ginn & Co.).—This appears to be an excellent text-book for high schools. The aim of the authors as stated in their preface has been to give "a simple and immediate presentation, in language which the student already understands, of the hows and whys of the physical world in which he lives." This idea has been consistently carried out; the explanations are lucid and free from technicalities; at the same time they are not generally open to the criticism which applies to many "simple" explanations, viz: that they are not true. In some cases the traditional order of subjects has been abandoned and the changes appear to be advantageous from the pedagogical point of view.

The illustrations are well-chosen and attractive, and the diagrams clear. H. A. B.

7. *A Laboratory Course in Physics for Secondary Schools;* by R. A. MILLIKAN and H. G. GALE. Pp. x + 134. New York 1906 (Ginn & Co.).—This is a collection of fifty-one experiments designed to accompany the text-book noticed above. The experiments are well chosen and clearly described; the necessary apparatus is simple in character and well designed for its purpose. H. A. B.

8. *Outlines of the Evolution of Weights and Measures and the Metric System;* by WILLIAM HALLOCK and HERBERT T. WADE. Pp. xi + 304. New York, 1906 (The Macmillan Co.).—The first chapter of this work gives an interesting outline of the historical development of metrology, so far as it is known, from the earliest times. The succeeding eight chapters have to do mainly with the metric system: its origin, development and extension throughout Europe; its advantages for commerce, manufacturing, engineering, medicine and pharmacy; and the international electrical units which have been derived from the fundamental metric units.

A final chapter deals with standards and methods of comparison and an appendix contains tables of equivalents and useful constants. H. A. B.

II. GEOLOGY.

1. *United States Geological Survey,* CHARLES D. WALCOTT, Director.—Titles of publications recently received are contained in the following list:

FOLIOS.—No. 138. Redding Folio, California. Description of the Redding quadrangle by J. S. DILLER. Pp. 14, with maps of topography and areal geology, structure and columnar sections.

No. 139. Snoqualmie Folio, Washington. Description of the Snoqualmie quadrangle by GEORGE OTIS SMITH and FRANK CATHCART CALKINS. Pp. 14, with maps of topography, areal geology, structure and columnar sections.

PROFESSIONAL PAPERS.—No. 50. The Montana Lobe of the Keewatin Ice Sheet; by FRED. H. H. CALHOUN. Pp. 62, with 7 plates and 31 figures.

BULLETINS.—No. 275. Slate Deposits and Slate Industry of the United States; by T. NELSON DALE, with sections by E. C. ECKEL, W. F. HILLEBRAND, and A. T. COONS. Pp. 154, with 25 plates and 15 figures.

No. 277. Mineral Resources of Kenai Peninsula, Alaska. Gold Fields of the Turnagain Arm Region; by FRED. H. MOFFIT. Coal Fields of the Kachemak Bay Region; by RALPH W. STONE. Pp. 80, with 18 plates and 5 figures.

No. 278. Geology and Coal Resources of the Cape Lisburne Region, Alaska; by ARTHUR J. COLLIER. Pp. 54, with 9 plates and 8 figures.

No. 284. Report on Progress of Investigations of Mineral Resources of Alaska in 1905; by ALFRED H. BROOKS and others. Pp. 169, with 14 plates and 10 figures.

No. 285. Contributions to Economic Geology, 1905; S. F. EMMONS, E. C. ECKEL, Geologists in charge. Pp. 506, with 13 plates and 16 figures.

No. 290. Preliminary Report on the Operations of the Fuel-testing Plant of the United States Geological Survey at St. Louis, Mo., 1905; JOSEPH A. HOLMES in charge. Pp. 240.

No. 291. A Gazetteer of Colorado; by HENRY GANNETT. Pp. 185.

WATER SUPPLY AND IRRIGATION PAPERS.—No. 155. Fluctuations of the Water Level in Wells, with Special Reference to Long Island, New York; by A. C. VEATCH. Pp. 83, with 9 plates and 17 figures.

No. 156. Water Powers of Northern Wisconsin; by LEONARD S. SMITH. Pp. 145, with 5 plates and 5 figures.

No. 158. Preliminary Report on the Geology and Underground Waters of the Roswell Artesian Area, New Mexico; by CASSIUS A. FISHER. Pp. 29, with 9 plates.

No. 160. Underground-Water Papers; MYRON L. FULLER, Geologist in charge. Pp. 104, with a map and 4 figures.

No. 162. Destructive Floods in the United States in 1905; by E. C. MURPHY and others. Pp. 105, with 4 plates and 11 figures.

No. 163. Bibliographic Review and Index of Underground-Water Literature published in the United States in 1905; by MYRON L. FULLER, FREDERICK G. CLAPP, and BERTRAND L. JOHNSON. Pp. 130.

Nos. 170, 172, 173, 174, 176, 178. Report of Progress of Stream Measurements for the Calendar year 1905. Prepared under the direction of F. H. NEWELL. Parts VI, VIII, IX, X, XII, XIV. Part. VI.—Great Lakes and St. Lawrence River Drainages; by R. E. HORTON, F. W. HANNA, and J. C. HOYT. Pp. 116, II, with one plate and two figures. Part VIII.—Missouri River Drainage; by C. C. BABB, M. C. HINDERLIDER and J. C. HOYT. Pp. 283, with one plate and 2 figures. Part IX.—Meramec, Arkansas and Lower Western Mississippi River Drainages; by M. C. HINDERLIDER, J. M. GILES and J. C. HOYT. Pp 103, with one plate and 2 figures. Part X.—Western Gulf of Mexico and Rio Grande Drainages; by T. W. TAYLOR and J. C. HOYT. Pp. 133, with one plate and 2 figures. Part XII.—The Great Basin Drainage; by M. C. HINDERLIDER, G. L. SWENDSEN, and HENRY THURTELL. Pp. 142, 11, with one plate and 2 figures. Part XIV.—Columbia River and Puget Sound Drainages; by D. W. ROSS, J. T. WHISTLER, and T. A. NOBLE. Pp. 250, II, with one plate and 2 figures.

List of the Publications of the United States Geological Survey. (Except Topographic Maps.) Pp. 58.

2. *Geologic Map of the Buffalo Quadrangle;* by D. D. LUTHER. Bull. 99, N. Y. State Mus., 1906, 29 pp. and map.—A general description is here given of the seventeen formations

outcropping in this quadrangle from the uppermost beds of the Silurian to the top of the Devonian. Diagnostic fossils for each formation are also listed. The map gives the areal distribution of the formations described. C. S.

3. *Second Report of the Director of the Science Division, 1905.* N. Y. State Mus., 1906, 99 pp.—This is the 59th report of the New York State Museum and the 2nd report of the Director of the Science Division, John M. Clarke. It deals with the work done and in preparation throughout the various divisions of the State Museum during the year 1905. Of particular interest to stratigraphers is the announcement,—"It is quite probable however that the Oswego sandstone [heretofore always accepted as Silurian] represents a near-shore condition, which was unfavorable for life, but farther west the Richmond fauna flourished under more suitable conditions." In other words, it is probable that the Oswego and Medina formations are the closing formations of the Ordovician. This is the view maintained by Ulrich of the U. S. Geological Survey, during the past three years, based on the Medina stratigraphy of the southern Appalachian.

Another striking correlation is that the Shawangunk conglomerate is not of Medina (Oneida) age, but "represents the invading basal member of the Salina formation in the eastern part of the State." C. S.

4. *The Upper Ordovician Rocks of Kentucky and their Bryozoa;* by JOHN M. NICKLES. Bull. 5, Kentucky Geol. Survey, 1905 (not received until July, 1906), 64 pp. and 3 pls.—This report describes the rocks of the Cincinnatian series and lists the Bryozoa of the various formations as found in Kentucky along the Cincinnati arch. Twenty-eight species are described, of which five are new. The illustrations show the macroscopic characters of the species. C. S.

5. *The Chazy Formation and its Fauna;* by P. E. RAYMOND. Ann. Carnegie Mus., iii, July, 1906, pp. 498–598.—This is the first article of a series of papers in which the author proposes to describe the stratigraphy and faunas of the Chazy as found in northeastern North America. The part now at hand deals with the stratigraphy of the various areas and lists of the fossils occurring in the various beds. The author's main conclusions are as follows:—

"This fauna shows a decidedly closer affinity with the fauna of the Black River and Trenton formations of New York and Canada than with the Beekmantown of the same regions. The strong Mohawkian facies of the Chazy fauna suggests that the Chazy formation should be taken out of the Canadian, the Beekmantown and Chazy having very little in common." There is but one species common to the two formations. "While the Black River and Trenton formations have only a few species in common with the Chazy, yet when the fossils are compared with one another it is found that almost every one in the Chazy is

represented in the Trenton by a very closely allied species" (p. 562). Thirteen new species are described. C. S.

6. *A New American Cybele;* by J. E. NARRAWAY and P. E. RAYMOND. Ann. Carnegie Mus., iii, July, 1906, pp. 599–604.—In America, this genus of trilobites is always rare and entire examples are almost unknown. The writers describe a nearly complete specimen preserving all the essential characters. It is named *Cybele ella*, and occurs in the Black River limestone of the Ordovician, near Ottawa, Canada. C. S.

7. *Uber Phylogenie der Arthropoden;* by A. HANDLIRSCH. Verh. k. k. zool.-bot. Gesellsch. Wien, 1906, pp. 88–103.—For several years, Handlirsch has had in preparation an octavo work entitled "Die Fossilen Insekten und die Phylogenie der Rezenten Formen,"* now being printed by Wilhelm Engelmann in Leipzig. From this work has resulted the paper under review.

The writer holds that the Arthropoda are monophyletic; that *Peripatus* stands much closer to the worms than to the true Arthropoda, and can not be regarded as the link uniting branchiate and tracheate Arthropoda. The stem group for all Arthropoda, he holds, must be sought among the trilobites. From these the Crustacea were first differentiated. The Arachnida are united with the trilobites through the limuloids, and with these the eurypteroids are closely related. The myriopods are seemingly difficult to derive from trilobites, but in the Carboniferous are many myriopod-like forms, the majority of which had a relatively broad and large head, with well-developed, large compound eyes like those of trilobites. Many of these forms were broad and had short segments in moderate numbers; some even had distinctly marked pleural parts quite similar to those in trilobites.

"From all these facts it seems clear that the primitive forms of myriopods were also relatively broad animals with homonomous segments, compound eyes, and cloven feet, living at least part of the time in water, and gradually adapted their breathing organs to a land existence. If we assume that the trilobites possessed nephridia on all segments, it is easily explained how in the very beginning two diverging myriopod-like stems originated, one of which had adapted the segmental organs situated far to the front, the other those far to the rear, to the service of sexual parts. In this event, the Progoneates and the Opisthogoneates are to be regarded as independent phyla" (p. 97).

This paper is of great interest to all students of the Arthropoda. C. S.

8. *Die Entwickelung von Indoceras baluchistanenense Noetling. Ein Beitrag zur Ontogenie der Ammoniten;* von F. NOETLING. Geol. u. Pal. Abh., Jena, viii, n. ser., 1906, pp. 1–96,

*Die Fossilen Insekten und die Phylogenie der Rezenten Formen. Ein Handbuch für Paläontologen und Zoologen; von Anton Handlirsch. I. Lieferung (mit 9 Tafeln). Pp. 160, Leipzig, 1906 (Wilhelm Engelmann).

7 plates.—This elaborate work describes in great detail the development of the highest Cretaceous ammonite mentioned in the title, and having a ceratite suture line. The development is as follows: (1) Protoconch stage; (2) Embryonic or Sphæroceras stage; (3) Metaconch or Oxynoticeras stage (has always five volutions irrespective of size of shell); (4) Paraconch or Indoceras stage.

The author concludes that on the basis of the developmental characters of the suture line alone it is at present not safe to decide as to the age of the strata in which the form occurs, for the reason that as yet we know the complete development of but few ammonites, and further that a primitive form may occur in young beds and a highly specialized species in old deposits.

In regard to the ancestry of *Indoceras*, the author concludes that "it had a different descent than *Sphenodiscus* or *Placenticeras* and that it can hardly be arranged with these in the family Pulchelliidæ, or with the Upper Cretaceous Oxynotus forms: *Garnieria*, *Lenticeras* and others are to be united in a family of indoceratids" (p. 92).

9. *Untersuchungen uber die Familie Lyttoniidae Waag. emend. Noetling;* von F. NOETLING. Palæontographica, li, 1906, pp. 129-153, pls. xv-xviii.—Some years ago, the author, while in India, collected in the Upper Permian of Chideru in the Salt Range an abundance of the genera *Oldhamina* and *Lyttonia*. As some of his specimens are preserved as silicious pseudomorphs, he was able through careful etching with hydrochloric acid to free them from the limestone and thus to reveal the entire structure of these remarkable and highly degenerate brachiopods. So strikingly aberrant are these forms that at first they were described as gasteropods (*Bellerophon*) and later as the teeth of fishes (*Leptodus*). The latter generic name Waagen displaced by his *Oldhamina* when he discovered these remains to be brachiopods. This proceeding is irregular, and it is to be regretted that Noetling does not return to *Leptodus*, especially after he remarks that according to the law of priority Waagen had no right to make this change (p. 133). On the other hand, *Oldhamina* can not be confused with *Oldhamia* even though the names sound nearly alike; and it is therefore further to be regretted that Noetling in a half-hearted way tries to dispossess the former by suggesting *Oldhamella*. The author prints the name in a foot-note (p. 129), and though it is only suggested, not seriously proposed, it can not be overlooked. Thus another synonym is added to the terminology of these shells. Some years ago he considered these fossils to be Bryozoa, and at that time proposed the name *Waagenopora*. Thus is literature burdened by giving way to printing all the unassimilated thoughts passing through an author's mind.

These shells are cemented to foreign bodies by the umbo of the ventral valve, and the scar of attachment is plainly preserved in young and apparently in adult specimens also (see pl.

xv, figs. 2a, 3). Because of the abnormal and very irregular lamellar thickenings of the posterior region of the shell margin (no two shells are alike in this character) covering over the scar of attachment, Noetling thinks these animals finally lost fixation and lay with the dorsal shell on the sea bottom.

He arrives at this conclusion because the majority of the specimens by far are ventral shells; some show the inner side of the dorsal valve and but a few preserve both valves in place. One might suppose that if the animal finally came to live as suggested by the author, all the specimens would preserve both valves, because after death, as the animal matter decayed, its place would be occupied by the "very soft calcareous mud" in which it lay. The reviewer thinks that during the weathering process the very thin dorsal shell is either dissolved away, or because of its deeply cleft nature and exterior papillose condition it adheres firmly to the outer rock, only to be dissolved away by weathering from this side. The fact that the mantle is constantly depositing shell on the outer posterior cardinal area is evidence that in some way it embraced foreign objects by which it held the shell in place. In old age such deposition may cease, but as these animals apparently lived in large communities they are nevertheless firmly held in place by their neighbors. On the other hand, if lying with the dorsal valve down in the soft mud, as suggested by the writer, it would seem that death must soon ensue through suffocation, because of the mud squeezing in through all of the many lateral clefts of the dorsal valve, but especially in preventing free water circulation with a fresh supply of food and oxygen.

Of the many cemented brachiopods, it is very rare to find one preserving the object of attachment, and on this account it should not be expected to occur here more than elsewhere. The reviewer believes that these animals lived with the deeply cleft dorsal valve uppermost, or that the posterior region of both valves lay somewhat embedded in the mud, with the greater portion of the anterior region protruding above the sea floor.

The author correctly removes these shells from the Thecidiidæ and regards them as more closely related to the Productidæ. He adds, "it may be that this aberrant group can even be included in this family so rich in forms" (p. 147). It seems now more probable that the Leptodidæ (new name) arose in some cemented form of the Productidæ, in which case it would be best looked for among *Strophalosia*. C. S.

III. Miscellaneous Scientific Intelligence.

1. *Les Prix Nobel en 1903.* Stockholm, 1906 (P. A. Norstedt & Söner).—The recipients of the Nobel prizes in 1903 were as follows: Henri Antoine Becquerel for his discovery of spontaneous radio-activity; Pierre and Marie Sklodovska Curie for their researches in the phenomena of radiation discovered by H. Becquerel; Svante August Arrhenius for the theory of electro-

lytic dissociation; Niels Ryberg Finsen for the treatment of diseases by light rays; Björnstjerne Björnsen for his poetical works. This interesting volume contains, in addition to an account of the ceremonies accompanying the prize distribution, biographical notices of the recipients with portraits and also reproductions of the Nobel medals and diplomas. The addresses at the *Conférences Nobel* by H. Becquerel, P. Curie, S. Arrhenius and W. Randal Cremer close the volume.

2. *British Association.*—The annual meeting of the British Association for the Advancement of Science was held at York from August 1 to 8; at which place the Association met both for the first time in 1831 and again in 1881. Prof. E. Ray Lankester in his presidential address reviewed the scientific advance of the past quarter century. The next meeting, for 1907, will be held in Leicester, that for 1908 in Dublin, and for 1909 at Winnipeg.

3. *Carnegie Institution of Washington.*—The following are titles of publications recently received:

No. 34. American Fossil Cycads; by G. R. Wieland. 4to. Pp. vii+296, 51 plates, 141 figures. A notice will follow.

No. 46. An Investigation into the Elastic Constants of Rocks, especially with reference to their Cubic Compressibility; by F. D. Adams and E. G. Coker. 8vo. Pp. 69, 16 plates. An abstract was published in the August number, pp. 95–123.

No. 50. The Relation of Desert Plants to Soil Moisture and to Evaporation; by Burton E. Livingston. Pp. 78, 16 cuts.

No. 52. Inheritance in Poultry (Paper No. 7, Station for Experimental Evolution); by C. B. Davenport. Pp. 136, 17 pl.

No. 53. Egyptological Researches; W. Max Müller. 4to. In press.

Obituary.

William Buck Dwight, Professor of Geology at Vassar College for nearly thirty years, died at Cottage City, Mass., on August 29, at the age of seventy-three years. He was born in Constantinople, the son of an American missionary, and came to this country in 1849. He was graduated at Yale College in 1854, at the Union Theological Seminary in 1857 and received the degree of B.S. from the Sheffield Scientific School in 1859. He carried on extensive field work in geology, chiefly in Dutchess County, N. Y., between 1879 and 1890; a number of papers giving his results are contained in this Journal. He invented a rock-slicing machine in 1891 and had charge of the department of geology in the Standard Dictionary. He was one of the original fellows of the Geological Society of America.

Dr. Paul Drude, Professor of Physics and Director of the Physical Laboratory at Berlin, died on July 5, at the age of forty-three years. He was the author of important theoretical and experimental researches on the electro-magnetic theory of light and since 1890 had been editor of the *Annalen der Physik*, during that period often known as Drude's Annalen.

Sir Walter Lawry Buller, well known for his work on the ornithology of New Zealand, died on July 19, at the age of sixty-eight years.

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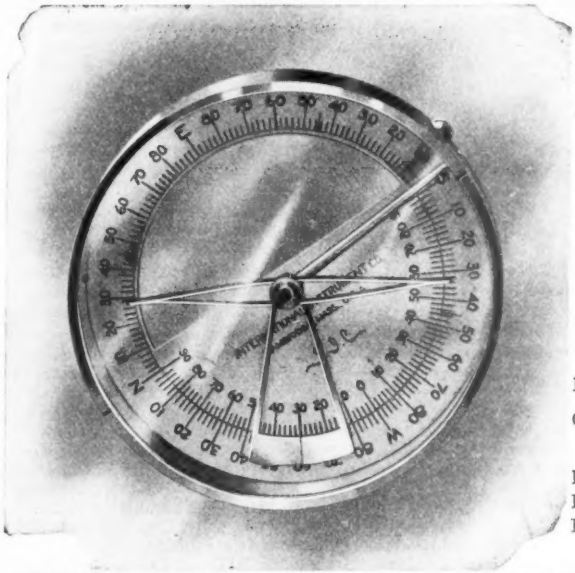

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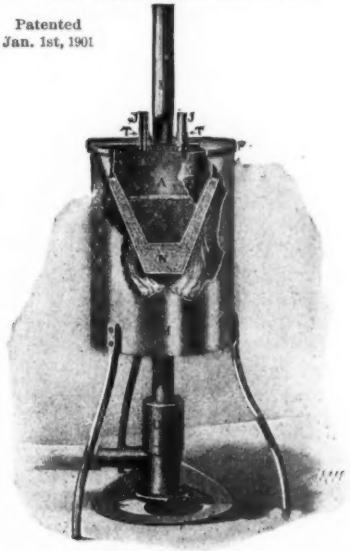

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